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A MATHEMATICAL DETERMINATION OF THE MAXIMUM PRESSURE AND THE EXTENT OF COMBUSTION IN THE GAS ENGINE

BY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY George Theodore Felbeck

ENTITLED A Mathematical Determination of the Maximum Pressure and the Extent of Combustion in the Gas Engine.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science in Mechanical Engineering.

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A Mathematical Determination of the Maximum Pressure and the Extent of Combustion in the Gas Engine

I. Introduction.

The maximum pressure obtained in the cylinder of a gas engine as measured from indicator cards is much less than one is led to expect from computations using the "air standard" cycle with air as a medium having constant specific heat. In fact, the actual pressures are about one-half those obtained by calculation. Some authorities claim that this discrepancy is due to the fact that the specific heat of the actual medium used in the gas engine increases with the temperature. Others maintain that combustion is incomplete and thus the pressure is lower. Some say that both causes contribute to the decrease in pressure.

To foretell with any degree of accuracy from theoretical considerations what the final result from a gaseous combustion will be the physical and chemical properties of the gases involved must be studied and not the properties of some other gas entirely foreign to the combustion under consideration. While air is one of the main constituents involved in the gas engine combustion process, the properties of the gaseous mixture are quite different from those of air. The gaseous mixture varies in different engines with the proportion of air to gas and with

the nature of the gas itself whether natural gas, producer gas, coal gas, or any of the other suitable gases. The physical and chemical properties of several different gaseous mixtures will in general be different although they may all have the same constituents. The properties of all the constituents are not the same so that when the proportions making up the gaseous mixture are changed the properties of the mixture as a whole are changed. It is not reasonable to suppose that all gaseous mixtures when burned under the same conditions as to initial pressure and temperature will all produce the same maximum pressure. Each case is a special one and no blanket calculation can be made to cover them all.

It is not fair, moreover, to an engine to measure its performance in terms of an ideal engine using a distinctly different medium such as air. To be able to judge the state of perfection of engine design the ideal established must be that which represents the maximum results obtainable with the given working medium.

II. Derivation of Energy Equation for Adiabatic Compression.

In this discussion only two phases of the Otto cycle will be taken up; namely, (1) compression and (2) combustion. Both processes will be considered adiabatic. At the beginning of compression the pressure will be taken as 14.7 lb. per square inch and the temperature as 190°F. Hopkinson*has shown that the temperature of the charge at the beginning of compression is in the neighborhood of 200°F. The value 190° has been chosen arbitrarily for convenience. It will be assumed that

*Proc. Inst. M.E. 1908, Vol. Jan. to May.

ignition takes place at the end of compression and that the combustion is instantaneous. The combustion will thus occur at constant volume. It will be assumed that the constituents of the gaseous mixture obey the perfect gas law PV/T = constant.* The following notation will be used:

State 1 (beginning of compression) P_1, V_1, T_1

State 2 (end of compression) P_2, V_2, T_2

State 3 (point of maximum pressure) P, V_2, T

P = lbs. per sq. ft. V = cu.ft. T = absolute °F.

The compression ratio V_1/V_2 is determined by the design of the engine. Knowing the compression ratio and with the assumption of $P_1 = 2116$ lbs.per sq.ft. and $T_1 = 650$, the values of P_2 and T_2 can be calculated from the following:

The energy equation

$$dq = du + A\,pdv \qquad (1)$$

becomes for the adiabatic case

$$du + Apdv = 0. \qquad (2)$$

Also we have

$$du = \gamma_v\,dt. \qquad (3)$$

Where γ_v is the instantaneous specific heat of the gas mixture per mol at constant volume.

The specific heat of a gas can be accurately represented as a function of the temperature for the range of temperature occurring in the gas engine. This function is of the following form:

$$\gamma_v = a_m + 2b_m T + 3f_m T^2 \qquad (4)$$

*For a discussion of the accuracy of this assumption, see British Association Committee Report, P.358,"Gas,Petrol and Oil Engines," by Dugald Clerk.

Combining (2), (3) and (4) we have

$$0 = (a_m + 2b_m T + 3f_m T^2)\,dT + Ap\,dv \qquad (5)$$

The perfect gas law gives

$$PV = M_1 RT \qquad (6)$$

where M_1 is the number of mols in the charge

$$P = \frac{M_1 RT}{V} \qquad (7)$$

Substituting (7) in (5) and dividing by T, we have

$$0 = \left(\frac{a_m}{T} + 2b_m + 3f_m T\right) dT + A M_1 R \frac{dv}{V} \qquad (8)$$

Integrating between the limits (1) and (2)

$$a_m \log_e \frac{T_2}{T_1} + 2b_m (T_2 - T_1) + \frac{3}{2} f_m (T_2^2 - T_1^2) = A M_1 R \log_e \frac{V_1}{V_2} \qquad (9)$$

It is sometimes more convenient to use the pressure relation P_2/P_1 than the volume relation V_1/V_2. From (6)

$$\frac{V_1}{V_2} = \frac{T_1}{T_2} \cdot \frac{P_2}{P_1} \qquad (10)$$

Then

$$\log_e \frac{V_1}{V_2} = \log_e \frac{T_1}{T_2} + \log_e \frac{P_2}{P_1} \qquad (11)$$

Substituting (11) in (9) and collecting terms we have

$$(a_m + A M_1 R) \log_e \frac{T_2}{T_1} + 2b_m (T_2 - T_1) + \frac{3}{2} f_m (T_2^2 - T_1^2) = A M_1 R \log_e \frac{P_2}{P_1} \qquad (12)$$

changing to common logarithms and dividing by the coefficient of the first term (12) becomes

$$\log_{10} \frac{T_2}{T_1} + \frac{2b_m}{2.3026(a_m + AM_1R)}(T_2 - T_1) + \frac{3f_m}{2 \cdot 2.3026(a_m + M_1AR)}(T_2^2 - T_1^2) = \frac{AM_1R}{a_m + AM_1R} \log_{10} \frac{P_2}{P_1} \qquad (13)$$

Transposing all known quantities to the right hand side of the equation, we have

$$\log_{10} T_2 + \frac{2b_m}{2.3026(a_m + AM_1R)} T_2 + \frac{3f_m}{2 \cdot 2.3026(a_m + AM_1R)} T_2^2 = \frac{AM_1R}{a_m + AM_1R} \log_{10} \frac{P_2}{P_1} + \log_{10} T_1 + \frac{2b_m}{2.3026(a_m + AM_1R)} T_1 + \frac{3f_m}{2 \cdot 2.3026(a_m + AM_1R)} T_1^2 \qquad (14)$$

Equation (14) can best be solved by trial for the unknown T_2.

The accuracy of the value of T_2 derived from equation (14) depends on the accuracy of the value taken for T_1 and upon the accuracy of the specific heat equation

$$\gamma_v = a + 2bT + 3fT^2$$

The value assumed for the temperature of the charge T may be accepted as accurate within 20° F. This temperature varies somewhat with the load but as the value 190°F was determined at full load and this treatment deals only with full load we need only one value for this suction temperature.

The equations for the specific heats that are available and that may be accepted as accurate for the range of temperatures encountered in the gas engine are as follows:

For the gases CO, O_2, N_2

$$\gamma_v = 4.51 + 0.5556\,\theta$$
$$\gamma_p = 6.5 + 0.5556\,\theta$$

For H_2

$$\gamma_v = 4.51 + 0.0005\,\theta$$
$$\gamma_p = 6.5 + 0.0005\,\theta$$

For CO_2

$$\gamma_v = 5.42 + 3.5\,\theta - 0.48\,\theta^2$$
$$\gamma_p = 7.41 + 3.5\,\theta - 0.48\,\theta^2$$

For H_2O

$$\gamma_v = 5.04 + 1.25\,\theta + 0.2\,\theta^2$$
$$\gamma_p = 7.03 + 1.25\,\theta + 0.2\,\theta^2$$

For C H_4

$$\gamma_v = 4.04 + 5.0\,\theta$$
$$\gamma_p = 6.03 + 5.0\,\theta$$

For C_2H_2

$$\gamma_p = 6.19 + 8.1\,\theta$$
$$\gamma_v = 4.20 + 8.1\,\theta$$

For C_2H_4

$$\gamma_p = 6.67 + 6.8\,\theta$$
$$\gamma_v = 4.68 + 6.8\,\theta$$

For C_2H_6

$$\gamma_p = 6.43 + 11.3\,\theta$$
$$\gamma_v = 4.44 + 11.3\,\theta$$

For C_6H_6 (vapor)

$$\gamma_p = 4.00 + 31.8\,\theta$$
$$\gamma_v = 2.01 + 31.8\,\theta$$

Where γ_v = instantaneous specific heat per mol at constant volume and $\theta = \frac{T}{1{,}000}$ where T = degrees Fahrenheit absolute.

For a discussion of specific heats see Appendix A.

While there are not sufficient specific-heat data to give accurately the variation of specific heat with temperature over any considerable range of temperature for acetylene (C_2H_2), ethylene (C_2H_4), Ethane (C_2H_6), and benzene (C_6H_6), a large error in the specific heat equations of these gases introduces no appreciable error in the calculation of the compression temperature.

Take for instance an engine running on acetylene (C_2H_2) with the theoretical required air:

Acetylene burns according to the reaction

$$C_2H_2 + 2\tfrac{1}{2}O_2 + 9.5N_2 \rightarrow 2CO_2 + H_2O + 9.5N_2$$

From the above reaction it is seen that the acetylene constitutes only 9.1% by volume of the original mixture. If the specific heat equation we use for acetylene gives results that are as high as 30% in error, the specific heat of the whole mixture is then only 3% in error. This error is less for the other hydrocarbons mentioned above because the ratio of required air to gas is greater than for acetylene. It is doubtful if any of the specific heat equations used give results which are correct to within 3%.

Knowing the compression pressure, temperature, and volume we have the initial conditions on which to base our calculations for the combustion phase.

III. Derivation of Equilibrium Equation for Constant Volume Adiabatic Combustion Involving Only the Reaction $CO + \frac{1}{2}O_2 \rightarrow CO_2$. Case I.

We will take first the case of an engine running on a simple gas such as CO. It will be assumed that none of the products of combustion of the previous cycle are left in thecylinder so that the initial charge consists only of carbon monoxide (CO), oxygen (O_2), and nitrogen (N_2).

Upon ignition of the charge it is possible for the following reactions to take place; namely,

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \qquad (1) \qquad\qquad N_2 + O_2 \rightarrow 2NO \qquad (2)$$

It will be shown later that reaction (2) does not take place to any appreciable extent so that it may be omitted from the discussion. (See Appendix D.)

Reaction (1) progresses until chemical equilibrium is established at which point we have the maximum pressure and temperature attainable in the given case. The proportions of the various gases present will remain the same until some change of pressure or temperature is made. This is what occurs when the engine piston moves forward. The gases expand doing useful work and the pressure and temperature decrease. At ordinary temperatures reaction (1) will go nearly to completion while at the high temperatures attained in the gas engine cylinder considerable CO and O_2 may be present. As the temperature decreases during expansion a greater part of the CO present burns to CO_2 so that at the point of exhaust the reaction is practically complete.

When a chemical reaction between two substances is first started the vigor of the reaction is great. Depending

on conditions, the reaction tends to go one way or the other. This tendency of the reaction to proceed we may call the driving force of the reaction. As the reaction proceeds this driving force decreases and the reaction slows up. When chemical equilibrium is established this driving force has been reduced to zero for there is no tendency for the reaction to proceed in either direction. If a reaction should acquire considerable momentum and proceed past the equilibrium point, the driving force becomes negative and the reaction is reversed and proceeds in the reversed direction until equilibrium is established.

We may represent a chemical reaction by fig.1. The point a represents the constituents in their initial state. Point b represents the reaction completed. Taking the reaction

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$

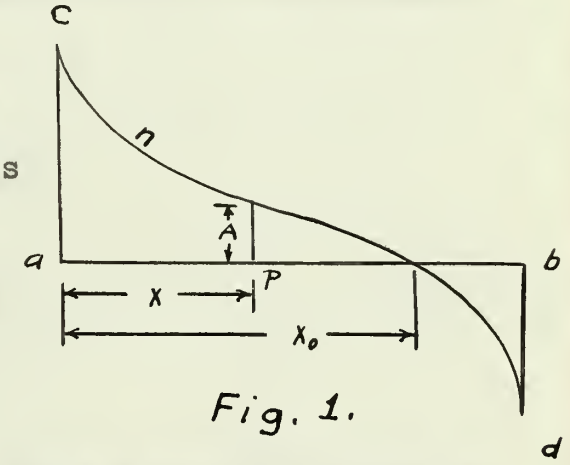


Fig. 1.

at point a we have only CO and O_2 while at point b there is only CO_2. The progress of the reaction is indicated by x. The ordinate of curve n is the driving force A of the reaction. The amount of mechanical work that can be done by the reaction up to any point P is represented by the area between curve n and the axis a,b between the limits a and x. This can be represented by the equation

$$_aW_x = \int_a^x A\,dx = E \qquad (15)$$

Differentiating eq.(15)

$$dW = A\,dx - dE$$

$$\frac{dE}{dx} = A \qquad (16)$$

From equation (16) the equilibrium point can be determined by putting $A = 0$. This equation involves the variable E and x. We may proceed as follows to express E in terms of x.

Since the laws of thermodynamics are applicable to chemical reactions we have the following:

$$dQ = du + dW = du + dE. \qquad (17)$$

dQ = heat from external sources

du = change in internal energy

dW = external work done dE.

Also for a reversible process,

$$dQ = TdS \qquad (18)$$

Combining (17) and (18),

$$dE = TdS - du \qquad (19)$$

Substituting (19) in (16) we have

$$T\frac{ds}{dx} - \frac{du}{dx} = A \qquad (20)$$

The variables S and u can be expressed in terms of T and x so that at a given temperature the value of x at the equilibrium point can be determined by putting $A = 0$ in equation (20). To transfer equation (20) into one involving x and T as variables we proceed as follows:

For the reaction under consideration; namely,

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$

the initial mixture is as follows using an e xcess of air,

	Mols
CO	1
O_2	e
N_2	f
sum	m

The gas mixture at any point x in the progress of the combustion is as follows:

	Mols
CO_2	x
CO	(1-x)
O_2	$(e-\frac{1}{2}x)$
N_2	f
sum	$m - \frac{1}{2}x = m'$

Let P be the pressure of the gas mixture in the state x; then the partial pressures of the consituents are

$$p_{CO_2} = \frac{x}{m'} P \qquad p_{O_2} = \frac{e-\frac{1}{2}x}{m'} P$$

$$p_{CO} = \frac{1-x}{m'} P \qquad p_{N_2} = \frac{f}{m'} P \qquad (21)$$

The energy U of the mixture is the sum of the energies of the constituents; that is,

$$U = xu_{CO_2} + (1-x)u_{CO} + (e-\tfrac{1}{2}x)u_{O_2} + fu_{N_2}$$

differentiating and multiplying by -1

$$-\frac{dU}{dx} = u_{CO} + \tfrac{1}{2}u_{O_2} - u_{CO_2} \qquad (22)$$

This expression is simply the heat of combustion H_v at constant volume and at the given constant temperature T. H_v varies with the temperature. Since the energy U is a point function it is independent of the path so that the same amount of heat is liberated in going direct from A to D as is evolved by taking the circuitous

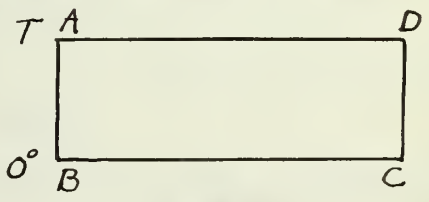


Fig. 2

path ABCD in fig. 2. Starting at point A with the initial gases at a temperature T the combustion is allowed to take place at constant temperature T. We then have

$$H_{v_T} = U_A - U_D$$

As a second process we first cool the initial gases down to absolute zero and then allow the combustion to take place at absolute zero so that

$$H_o = U_B - U_C$$

Finally the products of combustion are heated back up to T^o. The net result is the same as going direct from A to D. Then we may write

$$H_v = U_A - U_D = (U_A - U_B) + (U_B - U_C) - (U_D - U_C)$$

$$H_v = (U_A - U_B) + H_o - (U_D - U_C) \qquad (23)$$

$$U_A - U_B = \int_o^T \gamma_v dT$$

Let the instantaneous specific heats per mol at constant volume be as follows:

For CO, O_2, N_2

$$\gamma_v = a_1 + 2b_1 T + 3f_1 T^2$$

For CO_2

$$\gamma_v = a_2 + 2b_2 T + 3f_2 T^2$$

Then γ_v for original mixtures; i.e., CO with just sufficient oxygen

$$\gamma_v = \frac{3}{2}(a_1 + 2b_1 T + 3f_1 T^2)$$

$$U_A - U_B = \frac{3}{2}(a_1 T + b_1 T^2 + f_1 T^3) \qquad (24)$$

For final mixture after complete combustion; i.e., for 1 mol CO_2

$$\gamma_v = a_2 + 2b_2 T + 3f_2 T^2$$

Then

$$U_o - U_c = a_2 T + b_2 T^2 + f_2 T^3 \qquad (25)$$

Substituting (24) and (25) in (23)

$$-\frac{dU}{dx} = H = H \quad (\tfrac{3}{2}a - a)T \quad (\tfrac{3}{2}b - b)T \quad (\tfrac{3}{2}f - f)T \qquad (26)$$

The instantaneous specific heats of the gases are

$$\gamma_p = a_1' + 2b_1 T + 3f_1 T^2 \qquad a_1' = a_1 + AR'$$

$$\gamma_p = a_2' + 2b_2 T + 3f_2 T^2 \qquad a_2' = a_2 + AR' \qquad AR' = 1.99$$

The general expression for the entropy of a mol of gas is

$$s = s_o + \int \gamma_p \frac{dT}{T} - R \int \frac{dp}{p} \qquad R = 1.99$$

$$= s_o + a' \log T + 2bT + \tfrac{3}{2} fT^2 - R \log p \qquad (27)$$

Taking each of the constituents in the misture and multiplying the weight in mols by the expression (27) with appropriate constants and adding, the expression for the entropy of the mixture is

$$\begin{aligned} S = {} & x s_{o_{CO_2}} + (1-x) s_{o_{CO}} + (e - \tfrac{1}{2}x) s_{o_{O_2}} + f s_{o_{N_2}} \\ & + \left[x a_2' + (1-x) a_1' + (e - \tfrac{1}{2}x) a_1' + f a_1' \right] \log T \\ & + 2T \left[x b_2 + (1-x) b_1 + (e - \tfrac{1}{2}x) b_1 + f b_1 \right] \\ & + \tfrac{3}{2} T^2 \left[x f_2 + (1-x) f_1 + (e - \tfrac{1}{2}x) f_1 + f \cdot f_1 \right] \\ & - R \left[x \quad (1-x) \quad (e - \tfrac{1}{2}x) \quad f \right] \log P \\ & - R \left[x \log \frac{x}{m'} + (1-x) \cdot \log \left(\frac{(1-x)}{m} \right) + (e - \tfrac{1}{2}x) \cdot \log \left(\frac{e - \tfrac{1}{2}x}{m'} \right) + f \cdot \log \frac{f}{m'} \right] \end{aligned}$$

In getting the derivative $\frac{ds}{dx}$ it is convenient to take the six rows as separate functions, obtain their derivatives and add.

For the first row $\frac{d}{dx} = s_{o_{CO_2}} - s_{o_{CO}} - \frac{1}{2} s_{o_{O_2}} = -k \qquad (a)$

For the second row $\frac{d}{dx} = (a_2' - \frac{3}{2} a_1') \log T \qquad (b)$

For the third row $\frac{d}{dx} = 2(b_2 - \frac{3}{2}b_1)T$ (c)

For the fourth row $\frac{d}{dx} = \frac{3}{2}(f_2 - \frac{3}{2}f_1)T^2$ (d)

The fifth row is $-R(m-\frac{1}{2}x)\log P = -Rm' \log P$

Since the volume of the mixture remains constant during the reaction the pressure varies with x and in accordance with the following relation at any constant temperature T:

$$P = \frac{m-\frac{1}{2}x}{m'} P_a \qquad (27)$$

where P_a = pressure of mixture at temperature T with x = o

Therefore, $\log P = \log \frac{P}{m} + \log m'$

and the fifth now becomes

$$-Rm \log \frac{P}{m} - Rm \log m'$$

Taking out the term log m′ in the sixth row, that row becomes

$$R\left[m' \log m' - x \log x - (1-x) \log (1-x) - (e-\tfrac{1}{2}x)\log(e-\tfrac{1}{2}x) + f \log f\right]$$

Adding the fifth row the sum of the two is

$$-R\left[x \log x + (1-x) \log (1-x) + (e-\tfrac{1}{2}x) \log (e-\tfrac{1}{2}x) + f \log f + (m-\tfrac{1}{2}x) \log \frac{P_a}{m}\right]$$

The derivatives of this last expression are as follows:

Terms	Derivatives
$x \log x$	$\log x - 1$
$(1-x) \log (1-x)$	$-\log (1-x) - 1$
$(e-\frac{1}{2}x) \log (e-\frac{1}{2}x)$	$-\frac{1}{2} \log (e-\frac{1}{2}x) - \frac{1}{2}$
$(m-\frac{1}{2}x) \log \frac{P}{m}$	$-\frac{1}{2} \log \frac{P_a}{m} = \frac{1}{2} \log \frac{m-\frac{1}{2}x}{P}$

Grouped in a single expression

$$-R \log \frac{x}{1-x}\left(\frac{m-\frac{1}{2}x}{e-\frac{1}{2}x}\ \frac{1}{P}\right)^{\frac{1}{2}} + \tfrac{1}{2}R$$

Collecting all the derivatives, multiplying by T, and adding, we have the following:

$$T\frac{ds}{dx} = -kT - (\tfrac{3}{2}a_1' - a_2')T\log_e T - 2(\tfrac{3}{2}b_1 - b_2)T^2 - \tfrac{3}{2}(\tfrac{3}{2}f_1 - f_2)T^3 - RT\log\frac{x}{1-x}\left(\frac{m-\frac{1}{2}x}{e-\frac{1}{2}x}\cdot\frac{1}{P}\right)^{\frac{1}{2}} + \frac{1}{2}RT$$

From

$$-\frac{dU}{dx} = H_o + (\tfrac{3}{2}a_1' - a_2')T + (\tfrac{3}{2}b_1 - b_2)T^2 + (\tfrac{3}{2}f_1 - f_2)T^3$$

$$A = T\frac{ds}{dx} - \frac{dU}{dx} = H_o + T\left[\tfrac{1}{2}R + (\tfrac{3}{2}a_1' - a_2') - k\right] - (\tfrac{3}{2}a_1' - a_2')T\log_e T - (\tfrac{3}{2}b_1 - b_2)T^2 - \tfrac{1}{2}(\tfrac{3}{2}f_1 - f_2)T^3 - RT\log\frac{x}{1-x}\cdot\left(\frac{m-\frac{1}{2}x}{e-\frac{1}{2}x}\right)^{\frac{1}{2}}\cdot\frac{1}{P^{\frac{1}{2}}} \qquad (28)$$

$$\frac{x}{1-x}\left(\frac{m-\frac{1}{2}x}{e-\frac{1}{2}x}\cdot\frac{1}{P}\right)^{\frac{1}{2}} = \frac{\frac{x}{m'}P}{\frac{1-x}{m'}P\cdot\left(\frac{e-\frac{1}{2}x}{m'}P\right)^{\frac{1}{2}}} = \frac{P_{CO_2}}{P_{CO}\cdot P_{O_2}^{\frac{1}{2}}}$$

At equilibrium A = 0 and $\frac{P_{CO_2}}{P_{CO}\cdot P_{O_2}^{\frac{1}{2}}} = K_P$. Substituting these values in (28) we have

$$R\log_e K_P = \frac{H_o}{T} - (\tfrac{3}{2}a_1' - a_2')\log_e T - (\tfrac{3}{2}b_1 - b_2)T - \tfrac{1}{2}(\tfrac{3}{2}f_1 - f_2)T^2 + C \qquad (29)$$

Where $C = \tfrac{1}{2}R + (\tfrac{3}{2}a_1' - a_2') - k$.

Substituting the expression for K_P in terms of x we have

$$R\log_e\frac{x}{1-x}\left(\frac{m-\frac{1}{2}x}{e-\frac{1}{2}x}\right)^{\frac{1}{2}}\cdot\frac{1}{P^{\frac{1}{2}}} = \frac{H_o}{T} - (\tfrac{3}{2}a_1' - a_2')\log_e T - (\tfrac{3}{2}b_1 - b_2)T - \tfrac{1}{2}(\tfrac{3}{2}f_1 - f_2)T^2 + C \qquad (30)$$

From (27)

$$\frac{1}{P^{\frac{1}{2}}} = \left(\frac{m}{m-\frac{1}{2}x}\cdot\frac{1}{P_a}\right)^{\frac{1}{2}} = \left(\frac{m}{m-\frac{1}{2}x}\cdot\frac{T_2}{P_2T}\right)^{\frac{1}{2}} \qquad (30\text{ a.})$$

Substituting this in (30) we have

$$R\log_e\frac{x}{1-x}\left(\frac{m}{e-\frac{1}{2}x}\right)^{\frac{1}{2}}\cdot\left(\frac{T_2}{P_2T}\right)^{\frac{1}{2}} = \frac{H_o}{T} - (\tfrac{3}{2}a_1' - a_2')\log_e T - (\tfrac{3}{2}b_1 - b_2)T - \tfrac{1}{2}(\tfrac{3}{2}f_1 - f_2)T^2 + C \qquad (31)$$

The value of the constant of integration C can be calculated from equation (29) since values of K_P at various temperatures have been determined experimentally by various in-

vestigators. (See Appendix C.) Also the specific heat constants and the initial pressure P_2 and temperature T_2 are known so that for any given temperature T the progress x of the reaction can be calculated from equation (31).

IV. Derivation of Energy Equation for Case I.

In the problem of the gas engine, however, we do not know the temperature T so that for us equation (31) has two variables, T and x.

A second equation in T and x is necessary to determine the values of these two variables for the given constant volume gaseous combustion

This second equation is derived from a consideration of the thermal and chemical energies of the initial mixture and the mixture of gases at any point x during the progress of the reaction. In the states 2 and p, Fig. 3, we have as before the following gas mixtures.

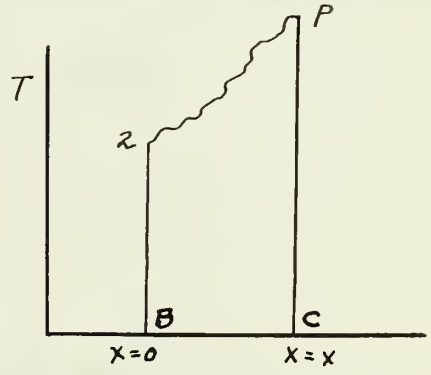


Fig. 3.

State 2.

	Mols
CO	1
O_2	e
N_2	f
	m

State p.

	Mols
CO_2	x
CO	1-x
O_2	$e-\frac{1}{2}x$
N_2	f
sum	$m-\frac{1}{2}x$

At the state 2 the total energy of the gas is made up of the thermal energy and the chemical energy. As the reaction proceeds to the point p, part of the heat of combustion is liberated and being an adiabatic process this heat of combustion serves to raise the temperature and consequently the

pressure of the gases within the cylinder of the engine.

The energy equation (1) holds for this process; namely, $dQ = dU + dW$.

Since the process is adiabatic

$$dQ = 0$$

and also occurs at constant volume

$$dW = 0$$

so that our energy equation becomes

$$dU = 0 \qquad (32)$$

Let us assume the following arbitrary path. First, cool the original mixture to absolute zero; second, let the reaction proceed to the point x at absolute zero; third, heat the gaseous mixture at x up to the temperature T at point p.

From (32), then,

$$(U_2 - U_B) + (U_B - U_C) + (U_C - U_P) = 0$$

$$U_B - U_C = U_P - U_C - (U_2 - U_B) \qquad (33)$$

$$U_B - U_C = xH_o$$

$$U_2 - U_B = m \int_o^{T_2} \gamma_v \, dT$$

$$\gamma_v = (a_1 + 2b_1 T + 3f_1 T^2)$$

$$U_2 - U_B = mT_2(a_1 + b_1 T_2 + f_1 T_2^2)$$

$$U_P - U_C = \int_o^T \left[(m - \tfrac{3}{2}x)\gamma_{V_1} + x\gamma_{V_2} \right] dT$$

$$(m - \tfrac{3}{2}x)\gamma_{V_1} + x\gamma_{V_2} = (m - \tfrac{3}{2}x)(a_1 + 2b_1 T + 3f_1 T^2) + x(a_2 + 2b_2 T + 3f_2 T^2)$$

$$U_P - U_C = (m - \tfrac{3}{2}x)T(a_1 + b_1 T + f_1 T^2) + xT(a_2 + b_2 T + f_2 T^2)$$

Substituting the above values in (33), we have

$$xH_o = (m - \tfrac{3}{2}x)T(a_1 + b_1 T + f_1 T^2) + xT(a_2 + b_2 T + f_2 T^2) - mT_2(a_1 + b_1 T + f_1 T^2)$$

Solving for x we have

$$x\left[H_o + T(a_1 + b_1 T + f_1 T^2) - T(a_2 + b_2 T + f_2 T^2)\right] = mT(a_1 + b_1 T + f_1 T^2) - mT_2(a_1 + b_1 T_2 + f_1 T_2^2)$$

$$x = \frac{m T(a_1 + b_1 T + f_1 T^2) - m T_2(a_1 + b_1 T_2 - f_1 T_2^2)}{H \quad T(a \; b \; T \; f \; T) - T(a \; b \; T \; f \; T)} \qquad (34)$$

Equations (31) and (34) determine x and T; that is, the conditions existing at the equilibrium point.

We derive P as follows from the law of perfect gases:

$$PV = m'RT$$

$$P_2V_2 = m\,RT_2$$

$$V = V_2$$

$$P = \frac{m'T}{m\,T_2}P_2$$

where $m' = m - \frac{1}{2}x$.

V. Numerical Example, Case I.

To illustrate the preceding points the following example is given:

Assume a gas engine running on an original mixture of CO with the theoretical amount of air. $P_1 = 14.7$ lb.per sq. in. absolute. $T_1 = 650^{\circ}$F; absolute. Compression pressure =150 lb. per sq. in absolute. Find the maximum pressure temperature and extent of combustion in the adiabatic Otto cycle.

Original mixture is

		Mols
CO	a	1.0
O_2	e	0.5
N_2	f	1.9
	m	= 3.4

For adiabatic compression we have equation (14) for which the constants are as follows:

$$a_m = 3.4 \times 4.51 = 15.334$$

$$2b_m = 3.4 \times 0.5556 \cdot 10^{-3} = 1.8890 \cdot 10^{-3}$$

$$f_m = 0$$

$AR = 1.985$

$mAR = 6.749$

Substituting the values for T, P, and P_2 equation (14) reduces to

$$\log_{10} T_2 + \left[\bar{5}.56995\right] T_2 = 3.14536$$

Brackets indicate logarithm of the coefficient.

By trial $T_2 = 1250^{\circ}$.

The constants for equation (34) which is the energy equation are as follows:

$a_1 = 4.51$	$a_2 = 5.42$	$H_o = 121,250$
$b_1 = 0.2778 \cdot 10^{-3}$	$b_2 = 1.75 \cdot 10^{-3}$	$m = 3.4$
$f_1 = 0$	$f_2 = -0.16 \cdot 10^{-3}$	$T_2 = 1225$

Using these constants equation (34) reduces to

$$x \quad \frac{3.4T(4.51 + 0.2778 \cdot 10^{-3} T) - 20,643}{121,250 + T(1.345 - 1.3333 \cdot 10^{-3} T + 0.16 \cdot 10^{-6} T^2)} \qquad (A)$$

By substitution the following pairs of values are obtained from equation (A):

T	5200	5300	5400	5500	5600
x	0.738	0.759	0.781	0.803	0.824

Equation (31) reduces to the following with the substitution of the proper constants: (See Appendix C.)

$$\log \frac{x}{1-x} \left(\frac{2m}{1-x}\right)^{\frac{1}{2}} = \frac{1}{4.571}\left[\frac{121,250}{T} - 5.3881 \log_{10} T + 1.335 \cdot 10^{-3} T - 0.08 \cdot 10^{-6} T^2 - 13.1 + \tfrac{1}{2}\left[\log \frac{P_2}{T_2} + \log T\right]\right] \qquad (B)$$

To obtain pairs of values from equation (B), assume a value of T which then definitely determines the value of the right hand member after which solution for x is accomplished by trial.

We have the following pairs of values from eq.(B):

T	5100	5200	5300	5400	5500
x	0.825	0.802	0.777	0.750	0.723

Plotting the values for T and x from equations (A) and (B) as shown in Fig. 4, page 19a, the intersection gives

$T = 5335 \qquad x = 0.767$

From equation (30 a.) we get

$$P = \frac{m - \frac{1}{2}x}{m} \cdot \frac{P_2 T}{T_2}$$

Substituting values

$$P = \frac{3.4 - \frac{0.767}{2}}{3.4} \cdot \frac{150 \cdot 5335}{1250}$$

$P = 568.1$ lb. per square inch.

VI. Derivation of Equilibrium Equations for Constant Volume Adiabatic Combustion Involving the Reactions $CO + \frac{1}{2}O_2 \rightarrow CO_2$ and $CO_2 \rightarrow CO + \frac{1}{2}O_2$ Case II.

In the case of the actual gas engine running on carbon monoxide and air we have the additional reaction $CO_2 \rightarrow CO + \frac{1}{2}O_2$ from the fact that some of the exhaust gases are left in the clearance space.

As the combustion proceeds, CO_2 is formed by the burning of the CO, and some of the CO_2 in the initial mixture is dissociated. We shall let x_1 denote the progress of the CO burning and $(1-x_2)$ be the progress of the CO_2 dissociation.

Initial Mixture	Mols	Intermediate Mixture	Mols
CO	a	CO_2	$ax_1 + gx_2$
O_2	e	CO	$a(1-x_1) + g(1-x_2)$
N_2	f	O_2	$e - \frac{1}{2}ax_1 + \frac{1}{2}g(1-x_2) = e'$
CO_2	g	N_2	f
	m		$m - \frac{1}{2}ax_1 + \frac{1}{2}g(1-x_2)$

Let E_1 be the reaction energy of the CO reaction.

" E_2 " " " " " " " CO_2 dissociation.

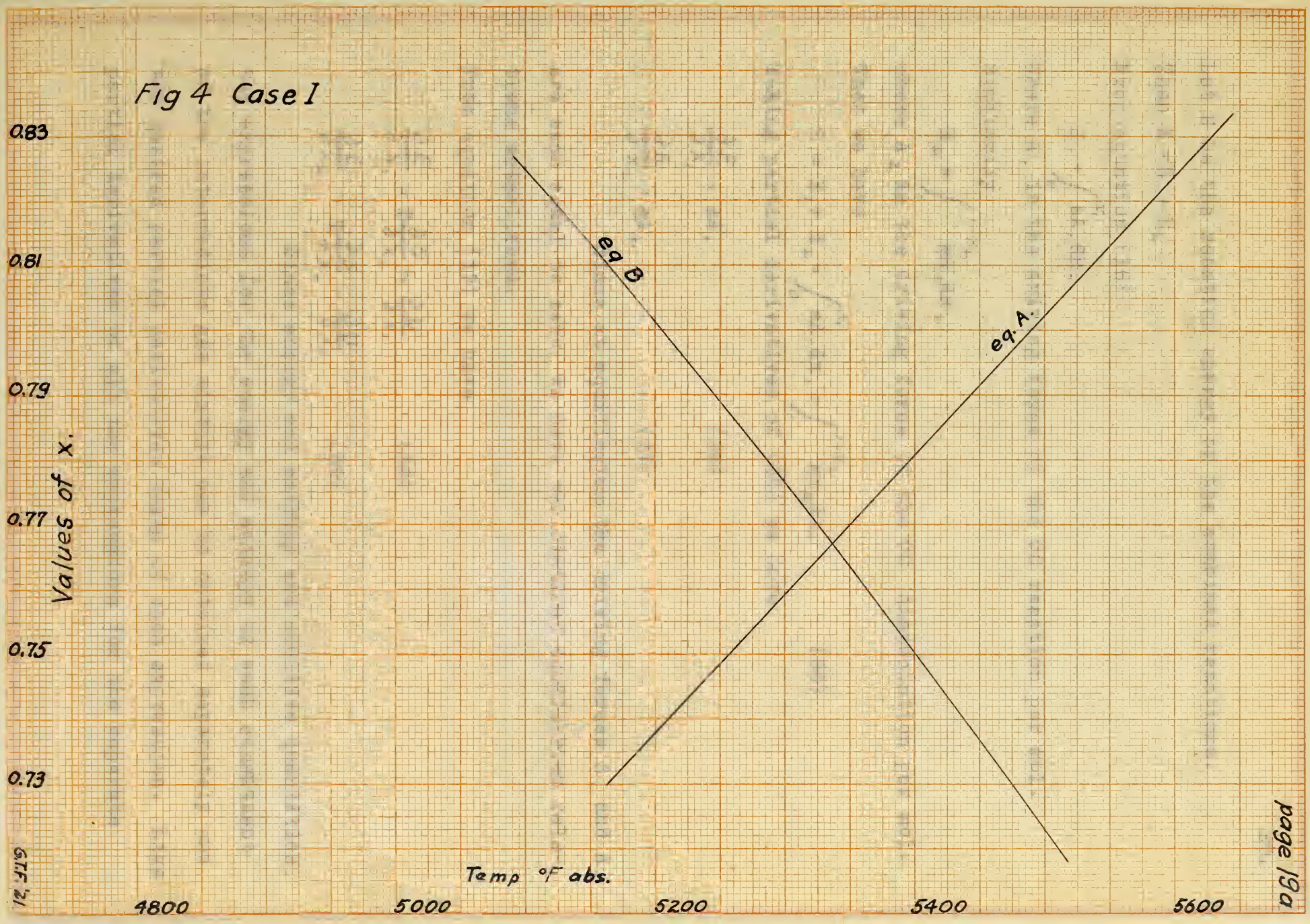


Fig 4 Case I
0.83
0.81
0.79
0.77
0.75
0.73
Values of x.
eq B
eq A.
4800
5000
5200
5400
5600
Temp °F abs.
page 19a

Let E be the reaction energy of the combined reactions.

Then $E = E_1 + E_2$

From equation (15)

$$E_1 = \int_0^{x_1} aA_1 dx_1$$

Where A_1 is the driving force of the CO reaction per mol.

Similarily

$$E_2 = \int_1^{1-x_2} gA_2 dx_2$$

where A_2 is the driving force of the CO dissociation per mol.

Then we have

$$E = E_1 + E_2 = \int_0^{x_1} aA_1 dx_1 + \int_1^{1-x_2} gA_2 dx_2 \qquad (35)$$

Taking partial derivatives of (35) we have

$$\frac{\partial E}{\partial x_1} = aA_1 \qquad (36)$$

$$\frac{\partial E}{\partial x_2} = gA_2 \qquad (37)$$

Since at equilibrium the driving forces A_1 and A_2 are each equal to zero, we have two distinct equilibrium relations established.

From equation (19) we have

$$\frac{\partial E}{\partial x_1} = T\frac{\partial S}{\partial x_1} - \frac{\partial U}{\partial x_1} \qquad (38)$$

$$\frac{\partial E}{\partial x_2} = T\frac{\partial S}{\partial x_2} - \frac{\partial U}{\partial x_2} \qquad (39)$$

Since energy and entropy are additive quantities, the expressions for the energy and entropy of each constituent of the intermediate gas mixture can be obtained separately and the desired partial derivatives taken of each expression. Like partial derivatives of all the expressions for the separate

constituents of the gas mixture when added together will give the partial derivatives of equations (38) and (39).

$$s_{CO_2} = \left[ax_1 + gx_2\right]\left[s_{o_{CO_2}} + a'_2 \log T + 2b_2 T + \tfrac{3}{2} f_2 T^2\right] - R\left[ax_1 + gx_2\right] \log \frac{ax_1 + gx_2}{m'} P \qquad (40)$$

Let $\phi_1 = a'_1 \log T + 2b_1 T + \frac{3}{2} f_1 T^2$

$\phi_2 = a'_2 \log T + 2b_2 T + \frac{3}{2} f_2 T^2$

From equation (27)

$$\frac{P}{m'} = \frac{P_a}{m}$$

Substituting these values in (40) we have

$$s_{CO_2} = \left[ax_1 + gx_2\right]\left[s_{o_{CO_2}} + \phi_2\right] - R\left[ax_1 + gx_2\right] \log \frac{ax_1 + gx_2}{m} P_a$$

$$\frac{\partial s_{CO_2}}{\partial x_1} = a\left[s_{o_{CO_2}} + \phi_2\right] - aR \log \frac{ax_1 + gx_2}{m'} P - aR$$

$$\frac{\partial s_{CO_2}}{\partial x_2} = g\left[s_{o_{CO_2}} + \phi_2\right] - gR \log \frac{ax_1 + gx_2}{m'} P - gR$$

For CO

$$S_{CO} = \left[a(1-x_1) + g(1-x_2)\right]\left[s_{o_{CO}} + \phi_1\right] - R\left[a(1-x_1) + g(1-x_2)\right] \log \frac{a(1-x_1) + g(1-x_2)}{m'} P$$

$$\frac{\partial s_{CO}}{\partial x_1} = -a\left[s_{o_{CO}} + \phi_1\right] + aR \log \frac{a(1-x) \; g(1-x)}{m} P + aR$$

$$\frac{\partial s_{CO}}{\partial x_2} = -g\left[s_{o_{CO}} + \phi_2\right] + gR \log \frac{a(1-x_1) + g(1-x_2)}{m'} P + gR$$

For O_2

$$S_{O_2} = \left[e - \tfrac{1}{2}ax_1 + \tfrac{1}{2}g(1-x_2)\right]\left[s_{o_{O_2}} + \phi_1\right] - R\left[e - \tfrac{1}{2}ax_1 + \tfrac{1}{2}g(1-x_2)\right] \log \frac{e - \frac{1}{2}ax_1 + \frac{1}{2}g(1-x_2)}{m'} P$$

$$\frac{\partial s_{O_2}}{\partial x_1} = -\tfrac{1}{2}a\left[s_{o_{O_2}} + \phi_1\right] + \tfrac{1}{2}aR \log \frac{e'}{m'} P + \tfrac{1}{2}aR$$

$$\frac{\partial s_{O_2}}{\partial x_2} = -\tfrac{1}{2}g\left[s_{o_{O_2}} + \phi_1\right] + \tfrac{1}{2}gR \log \frac{e'}{m'} P + \tfrac{1}{2}gR$$

For N

$$\frac{\partial s_{N_2}}{\partial x_1} = 0 \qquad \frac{\partial s_{N_2}}{\partial x_2} = 0$$

The energy equation for the total intermediate mixture is

$$U = u_{co_2}\left[ax_1 + gx_2\right] + u_{co}\left[a(1-x_1) + g(1-x_2)\right] + u_{o_2}\left[e - \tfrac{1}{2}ax_1 + \tfrac{1}{2}g(1-x_2)\right] + fu_{N_2}$$

$$-\frac{\partial U}{\partial x_1} = a\left[u_{co} + \tfrac{1}{2}u_{o_2} - u_{co_2}\right] = a H_v$$

$$-\frac{\partial U}{\partial x_2} = g\left[u_{co} + \tfrac{1}{2}u_{o_2} - u_{co_2}\right] = g H_v$$

Collecting the various results we have

$$\frac{1}{a}\left[T\frac{\partial S}{\partial x_1} - \frac{\partial U}{\partial x_1}\right] = H_v + T\left[S_{o_{co_2}} + \phi_2 - R\log\frac{ax_1 + gx_2}{m'}P - R\right]$$

$$+T\left[-S_{o_{co}} + \phi_1 + R\log\frac{a(1-x_1) + g(1-x_2)}{m'}P + R\right]$$

$$+T\left[-\tfrac{1}{2}S_{o_2} - \tfrac{1}{2}\phi_1 + \tfrac{1}{2}R\log\frac{e'}{m'}P + \tfrac{1}{2}R\right] \quad (39a)$$

$$\frac{1}{a}\left[T\frac{\partial S}{\partial x_1} - \frac{\partial U}{\partial x_1}\right] = H_v - (k - \tfrac{1}{2}R)T + (\phi_2 - \tfrac{3}{2}\phi_1)T - RT\log\frac{ax_1 + gx_2}{a(1-x_1) + g(1-x_2)}\left(\frac{m'}{e'P}\right)^{\frac{1}{2}} \quad (40a)$$

$$\frac{1}{g}\left[T\frac{\partial S}{\partial x_2} - \frac{\partial U}{\partial x_2}\right] = \text{same expression.}$$

From (39 a) and (40 a)

$$\frac{1}{a}\left[T\frac{\partial S}{\partial x_1} - \frac{\partial U}{\partial x_1}\right] = \frac{1}{g}\left[T\frac{\partial S}{\partial x_2} - \frac{\partial U}{\partial x_2}\right]$$

or $$\frac{1}{a}\frac{\partial E}{\partial x_1} = \frac{1}{g}\frac{\partial E}{\partial x_2}$$

From (36) and (37)

$$\frac{\partial E}{\partial x_1} = aA_1 \qquad \frac{\partial E}{\partial x_2} = gA_2$$

Combining these with equation (41) we have

$$A_1 = A_2$$

If the driving forces of two reactions are equal, then under the same conditions the two reactions will establish the same equilibrium.

Therefore at equilibrium

$$X_1 = X_2 = X$$

From equation (39) at equilibrium we have

$$0 = H_v - (k - \tfrac{1}{2}R)T + (\phi_2 - \tfrac{3}{2}\phi_1)T - RT \log \frac{X}{1-X}\left(\frac{m'}{e'P}\right)^{\frac{1}{2}}$$

$$\frac{X}{1-X}\left(\frac{m'}{e'P}\right)^{\frac{1}{2}} = \frac{\frac{(a+g)X}{m'}P}{\frac{(a+g)\,1-X}{m'}P\left(\frac{e'}{m'}P\right)^{\frac{1}{2}}} = \frac{P_{CO_2}}{P_{CO}\cdot P_{O_2}^{\frac{1}{2}}} = K_P$$

$$\therefore R \log_e K_P = \frac{H_v}{T} - (k - \tfrac{1}{2}R) + (\phi_2 - \tfrac{3}{2}\phi_1)$$

Substituting the expressions for ϕ_1 and ϕ_2

$$R \log_e K_P = \frac{1}{T}\Big[H_0 + (\tfrac{3}{2}a_1 - a_2)T + (\tfrac{3}{2}b_1 - b_2)T^2 + (\tfrac{3}{2}f_1 - f_2)T^3 + a_2' \log T + 2b_2 T + \tfrac{3}{2}f_2 T^2 - \tfrac{3}{2}a_1' \log T - 3b_1 T - \tfrac{9}{4}f_1 T^2 - (k - \tfrac{1}{2}R)\Big]$$

Collecting terms

$$R \log_e K_P = \frac{H_0}{T} - (\tfrac{3}{2}a_1' - a_2') \log T - (\tfrac{3}{2}b_1 - b_2)T - \tfrac{1}{2}(\tfrac{3}{2}f_1 - f_2)T^2 - \left[k - \tfrac{1}{2}R - (\tfrac{3}{2}a_1 - a_2)\right]$$

The above equation is identical with equation (29). The equilibrium relation between x and T is therefore

$$R \log_e \frac{X}{1-X}\left(\frac{m}{e + \frac{1}{2}g - \frac{1}{2}(a+g)X}\right)^{\frac{1}{2}}\left(\frac{T_2}{P_2 T}\right)^{\frac{1}{2}} = \frac{H_0}{T} - \frac{3}{2}(a_1' - a_2') \log T - (\tfrac{3}{2}b_1 - b_2)T - \tfrac{1}{2}(\tfrac{3}{2}f_1 - f_2)T^2 + C \qquad (42)$$

VII. Derivation of Energy Equation Case II.

The energy relation between x and T is

$$a x H_0 + g(1-x)H_0 = (a+g)\,x\,T(a_2 + b_2 T + f_2 T^2) + \left[m + \tfrac{1}{2}g - \tfrac{3}{2}(a+g)\,x\right]T\left[a_1 + b_1 T + f_1 T^2\right] - u_2$$

$$u_2 = (a+e+f)\,T_2(a_1 + b_1 T_2 + f_1 T_2^2) + g T_2 (a_2 + b_2 T_2 + f_2 T_2^2)$$

$$x\left[(a+g)H_0 - (a+g)T(a_2 + b_2 T + f_2 T^2) + \tfrac{3}{2}(a+g)T(a_1 + b_1 T + f_1 T^2)\right] = g H_0 - u_2 + (m + \tfrac{1}{2}g)\,T(a_1 + b_1 T + f_1 T^2)$$

$$X = \frac{\frac{g H_0 - u_2}{T} + (m + \tfrac{1}{2}g)\,T(a_1 + b_1 T + f_1 T^2)}{(a+g)\left[\frac{H_0}{T} - (a_2 + b_2 T + f_2 T^2) + \tfrac{3}{2}(a_1 + b_1 T + f_1 T^2)\right]} \qquad (43)$$

The solution of equations (42) and (43) gives x and T for the combustion of the gaseous mixture containing CO, CO_2, O_2 and N_2.

VIII. Numerical Example Case II.

The following example illustrates the procedure:

A gas engine runs on CO using the theoretical amount of air. $P_1 = 14.7$ lb. per square inch absolute. $T_1 = 650^{\circ}$F. absolute. $P_2 = 150$ lb. per square inch (abs). Assume that 10% of the products of combustion are left in the clearance space. Find the maximum pressure, temperature, and extent of combustion in the adiabatic Otto cycle.

The original mixture in the cylinder is as follows:

	Mols	
CO	1.00	a
O_2	0.50	e
N_2	2.09	f
CO_2	0.10	g
	3.69 =	m

The constants for the adiabatic compression equation are

$a_m = 3.59 \cdot 4.51 + 0.10 \cdot 5.42 = 16.633$

$2b_m = 3.59 \cdot 0.5556 \cdot 10^{-3} + 0.10 \cdot 3.5 \cdot 10^{-3} = 2.345 \cdot 10^{-3}$

$\frac{3}{2} f_m = -0.10 \frac{0.48}{2} \cdot 10^{-6} = -0.024\ 10$

$mAR = 3.69 - 1.985 = 7.325$

$a_m + mAR = 23.958$

Substituting these constants and the values for P_1, T, and P_2 in equation (14) we have: (Brackets indicate logarithm of the coefficient.)

$$\log_{10} T_2 + \left[\overline{5}.62847\right] T_2 - \left[\overline{10}.63854\right] T_2^2 = 3.14879$$

By trial $T_2 = 1250^{\circ}$F. absolute.

Substituting the numerical values for the constants in equation (43) we have

$$X = \frac{\frac{-10.589}{T} + 3.74(4.51 + 0.2778 \cdot 10^{-3} T)}{1.10\left[\frac{121250}{T} + 1.345 - 1.3333 \cdot 10^{-3} T + 0.16 \cdot 10^{-6} T^2\right]} \quad (C)$$

By substitution we get from equation (c)

T	5100	5200	5300	5400
x	0.810	0.834	0.855	0.877

Substituting numerical constants in equation (42) we have

$$\log \frac{X}{(1-X)^{3/2}} = \frac{1}{4.571} \log K_P + \frac{1}{2}\left[\log \frac{150 \cdot 144 \cdot 0.55}{1250 \cdot 3.69} + \log T\right]$$

$$\log \frac{X}{(1-X)^{3/2}} = \frac{1}{4.571} \log K_P + \frac{1}{2} \log T + 0.20545$$

By substitution from equation (D)

T	5100	5200	5300	5400	5500
x	0.826	0.802	0.778	0.751	0.724

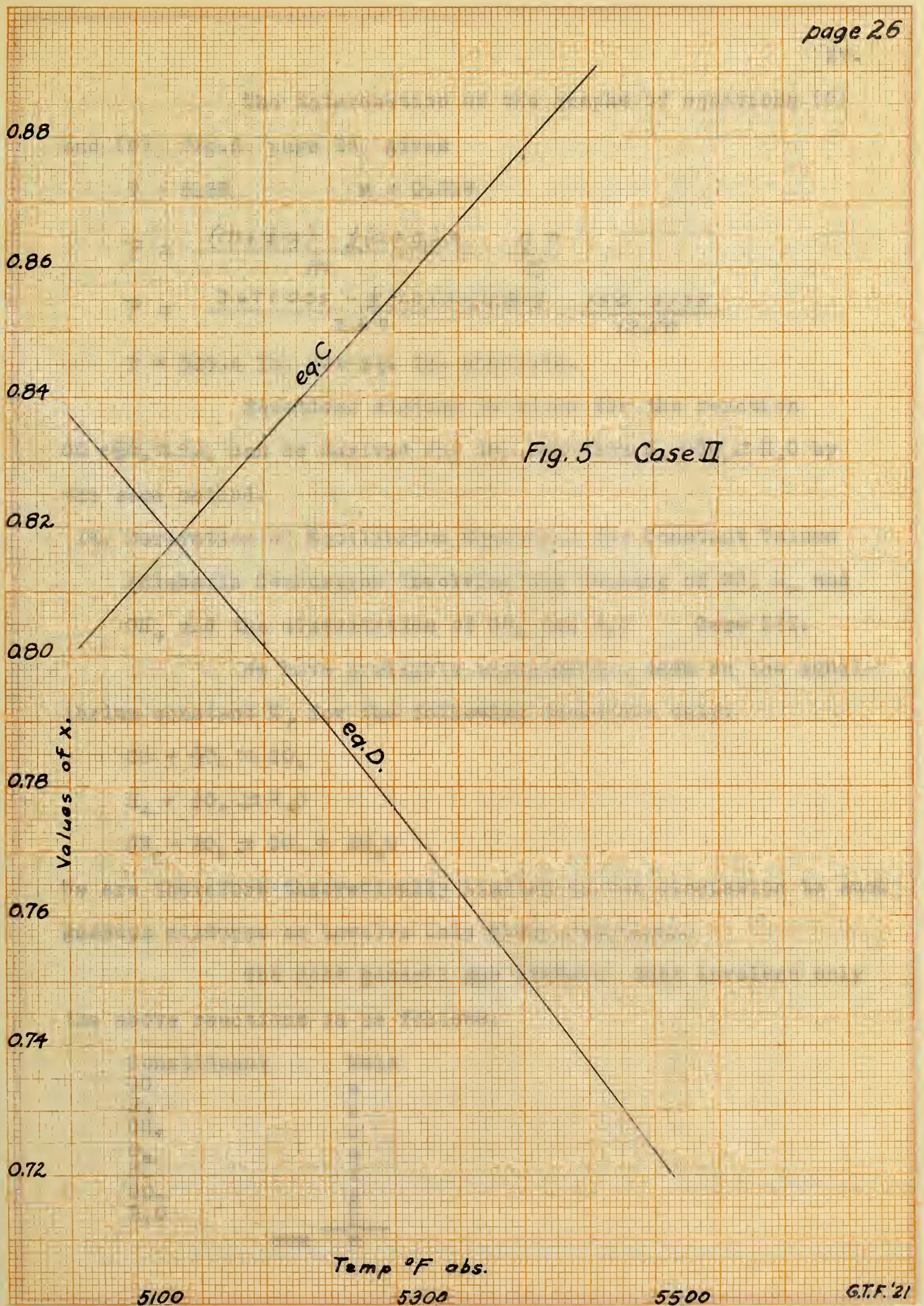

0.88
0.86
0.84
0.82
0.80
0.78
0.76
0.74
0.72
eq. C
eq. D.
Values of x.
Temp °F abs.
5100
5300
5500
G.T.F. '21

Fig. 5 Case II

Fig. 5 Case II
Temp °F abs.
Values of x

The intersection of the graphs of equations (C) and (D), fig.5, page 26, gives

$T = 5135 \qquad x = 0.819$

$$P = \frac{(m+\frac{1}{2}g) - \frac{1}{2}(a+g)x}{m} \cdot \frac{P_2 T}{T_2}$$

$$P = \frac{3.69 + 0.05 - \frac{1}{2}(1.0+0.1)0.819}{3.69} \cdot \frac{150 \cdot 5135}{1250}$$

P = 549.4 lb. per sq. in. absolute.

Equations similar to those for the reaction $CO + \frac{1}{2}O_2 \leftrightharpoons CO_2$ can be derived for the reaction $H_2 + \frac{1}{2}O_2 \rightleftarrows H_2O$ by the same method.

IX. Derivation of Equilibrium Equations for Constant Volume Adiabatic Combustion Involving the Burning of CO, H_2 and CH_4 and the dissociation of CO_2 and H_2O Case III.

We have available experimental data on the equilibrium constant K_p for the following reactions only:

$$CO + \tfrac{1}{2}O_2 \leftrightharpoons CO_2$$

$$H_2 + \tfrac{1}{2}O_2 \rightleftarrows H_2O$$

$$CH_4 + 2O_2 \rightleftarrows CO_2 + 2H_2O$$

We are therefore theoretically limited in our discussion to such gaseous mixtures as involve only these reactions.

The most general gas mixture that involves only the above reactions is as follows:

Constituent	Mols
CO	a
H_2	b
CH_4	c
O_2	e
N_2	f
CO_2	g
H_2O	h
sum	m

In the combustion of the methane constituent of the above gas CO_2 and H_2O will be the products. At the high temperature produced some of this CO_2 and also the H_2O will dissociate so that in reality the products of combustion of CH_4 are CO_2, H_2O, CO, H_2, and O_2.

We shall use the following variables to denote the progress of the various reactions:

(1) x_1, progress of CO reaction

(2) y_1 " " H_2 "

(3) z " " CH_4 "

(4) $(1-x_2)$ " " CO_2 dissociation

(5) $(1-y_2)$ " " H_2O "

(6) $(1-x_3)$ " " CO_2 ")Produced by CH_4 combus-

(7) $(1-y_3)$ " " H_2O ")tion

In determining the intermediate mixture consider first the CH_4 combustion.

$$(c)CH_4 + (2c)O_2 \rightarrow (2cz)H_2O + (cz)CO_2 + c(1-z)CH_4$$

$$(2cz)H_2O \rightarrow 2cz\left[y_3 H_2O + \tfrac{1}{2}(1-y_3)O_2 + (1-y_3)H_2\right]$$

$$(cz)CO_2 \rightarrow cz\left[x_3 CO_2 + \tfrac{1}{2}(1-x_3)O_2 + (1-x_3)CO\right]$$

We have from the various processes of the combustion the following:

	H_2	CO	O_2	CO_2	H_2O	CH_4
1st reaction	---	$a(1-x_1)$	$-\frac{1}{2}ax_1$	ax_1	---	---
2nd "	$b(1-y_1)$	---	$-\frac{1}{2}by_1$	---	by_1	---
3rd "	---	---	$-2cz$	---	---	$c(1-z)$
4th disso.	---	$g(1-x_2)$	$\frac{1}{2}g(1-x_2)$	gx_2	---	---
5th "	$h(1-y_2)$	---	$\frac{1}{2}h(1-y_2)$	---	hy_2	---
6th "	---	$cz(1-x_3)$	$\frac{1}{2}cz(1-x_3)$	czx_3	---	---
7th "	$2cz(1-y_3)$	---	$cz(1-y_3)$	---	$2czy_3$	---

Collecting terms we have for our intermediate mixture:

CO_2	$ax_1 + gx_2 + czx_3$
H_2O	$by_1 + hy_2 + 2czy_3$
CH_4	$c(1-z)$
CO	$a(1-x_1)+g(1-x_2)+cz(1-x_3)$
H_2	$b(1-y_1)+h(1-y_2)+2cz(1-y_3)$
O_2	$e+\frac{1}{2}a(1-x_1)+\frac{1}{2}b(1-y_1)+\frac{1}{2}g(1-x_2)+\frac{1}{2}h(1-y_2)+\frac{1}{2}cz(1-x_3)$ $+cz(1-y_3)-2cz-\frac{1}{2}(a+b) = e'$
N_2	f
	sum $= m'$

Since the reaction energy of the total is the sum of the reaction energies of the reactions of the various constituents, we have

$$dE = A_1dx_1 + A_2dx_2 + A_3dx_3 + A_4dy_1 + A_5dy_2 + A_6dy_3 + A_7dz \quad (44)$$

Then

$$\frac{\partial E}{\partial x_1} = A_1 \quad \frac{\partial E}{\partial x_2} = A_2 \quad \frac{\partial E}{\partial x_3} = A_3 \quad \frac{\partial E}{\partial y_1} = A_4 \quad \frac{\partial E}{\partial y_2} = A_5$$

$$\frac{\partial E}{\partial y_3} = A_6 \quad \frac{\partial E}{\partial z} = A_7 \quad (45)$$

Also, as before

$$dE = TdS - dU$$

then

$$\frac{\partial E}{\partial x_1} = T\frac{\partial S}{\partial x_1} - \frac{\partial U}{\partial x_1} \quad \text{etc.}$$

Let

$\phi_1 = a_1' \log T + 2b_1 T + \frac{3}{2}f_1 T$ i.e. for N_2, O_2, and CO.

$\phi_2 = a_2' \log T + 2b_2 T + \frac{3}{2}f_2 T$ i.e. for CO_2.

$\phi_3 = a_3' \log T + 2b_3 T + \frac{3}{2}f_3 T$ i.e. for H_2O.

$\phi_4 = a_4' \log T + 2b_4 T + \frac{3}{2}f_4 T$ i.e. for CH_4.

$\phi_5 = a_5' \log T + 2b_5 T + \frac{3}{2}f_5 T$ i.e. for H_2.

For the CO_2 constituent

$$S_{CO_2} = [ax_1 + gx_2 + czx_3][S_{oCO_2} + \phi_2]$$

$$-R[\quad " \quad]\log\left[\frac{ax_1 + gx_2 + czx_3}{m'}P\right]$$

$$\frac{\partial S_{CO_2}}{\partial x_1} = a[S_{oCO_2} + \phi_2] - aR\log[\quad " \quad] - aR$$

$$\frac{\partial S_{CO_2}}{\partial x_2} = g[\quad " \quad] - gR\log[\quad " \quad] - gR$$

$$\frac{\partial S_{CO_2}}{\partial x_3} = cz[\quad " \quad] - czR\log[\quad " \quad] - czR$$

$$\frac{\partial S_{CO_2}}{\partial z} = cx_3[\quad " \quad] - cx_3R\log[\quad " \quad] - cx_3R$$

For the H_2O constituent

$$S_{H_2O} = [by_1 + hy_2 + 2czy_3][S_{oH_2O} + \phi_3]$$

$$-R[\quad " \quad]\log\left[\frac{by_1 + hy_2 + 2czy_3}{m'}P\right]$$

$$\frac{\partial S_{H_2O}}{\partial y_1} = b[S_{oH_2O} + \phi_3] - bR\log[\quad " \quad] - bR$$

$$\frac{\partial S_{H_2O}}{\partial y_2} = h[\quad " \quad] - hR\log[\quad " \quad] - hR$$

$$\frac{\partial S_{H_2O}}{\partial y_3} = 2cz[\quad " \quad] - 2czR\log[\quad " \quad] - 2czR$$

$$\frac{\partial S_{H_2O}}{\partial z} = 2cy_3[\quad " \quad] - 2cy_3R\log[\quad " \quad] - 2cy_3R$$

For the CH_4 constituent,

$$S_{CH_4} = c(1-z)[S_{oCH_4} + \phi_4] - c(1-z)R\log\frac{c(1-z)}{m'}P$$

$$\frac{\partial S_{CH_4}}{\partial z} = -c[S_{oCH_4} + \phi_4] + cR\log\frac{c(1-z)}{m'}P + cR$$

For the CO constituent

$$S_{co} = [a(1-x_1)+g(1-x_2)+cz(1-x_3)][S_{oco}+\phi_{18}]$$
$$-R[\quad\text{"}\quad]\log\left[\frac{a(1-x_1)+g(1-x_2)+cz(1-x_3)}{m'}P\right]$$
$$\frac{\partial S_{co}}{\partial x_1} = -a\,[S_{oco}+\phi_1] + aR\log[\quad\text{"}\quad] + aR$$
$$\frac{\partial S_{co}}{\partial x_2} = -g\,[\quad\text{"}\quad] + gR\log[\quad\text{"}\quad] + gR$$
$$\frac{\partial S_{co}}{\partial x_3} = -cz\,[\quad\text{"}\quad] + czR\log[\quad\text{"}\quad] + czR$$
$$\frac{\partial S_{co}}{\partial Z} = +c(1-x_3)[\quad\text{"}\quad] - c(1-x_3)R\log[\quad\text{"}\quad] - c(1-x_3)R$$

For the H_2 constituent,

$$S_{H_2} = [b(1-y_1)+g(1-y_2)+2cz(1-y_3)][S_{oH_2}+\phi_5]$$
$$-R[\quad\text{"}\quad]\log\left[\frac{b(1-y_1)+h(1-y_2)+2cz(1-y_3)}{m'}P\right]$$
$$\frac{\partial S_{H_2}}{\partial y_1} = -b\,[S_{oH_2}+\phi_5] + bR\log[\quad\text{"}\quad] + bR$$
$$\frac{\partial S_{H_2}}{\partial y_2} = -h\,[\quad\text{"}\quad] + hR\log[\quad\text{"}\quad] + hR$$
$$\frac{\partial S_{H_2}}{\partial y_3} = -2cz\,[\quad\text{"}\quad] + 2czR\log[\quad\text{"}\quad] + 2czR.$$
$$\frac{\partial S_{H_2}}{\partial Z} = 2c(1-y_3)[\quad\text{"}\quad] - 2c(1-y_3)R\log[\quad\text{"}\quad] - 2c(1-y_3)R$$

For the O_2 constituent

$$e' = e+\tfrac{1}{2}a(1-x_1)+\tfrac{1}{2}b(1-y_1)+\tfrac{1}{2}g(1-x_2)+\tfrac{1}{2}h(1-y_2)+\tfrac{1}{2}cz(1-x_3)$$
$$+cz(1-y_3)-2cz-\tfrac{1}{2}(a+b)$$

$$S_{O_2} = e'\left[S_{oo_2} + \phi_1\right] - e'\left[R \log \frac{e'}{m'} P\right]$$

$$\frac{\partial S_{O_2}}{\partial x_1} = -\tfrac{1}{2}a\left[\quad " \quad\right] + \tfrac{1}{2}a\left[\quad " \quad\right] + \tfrac{1}{2}aR$$

$$\frac{\partial S_{O_2}}{\partial x_2} = -\tfrac{1}{2}g\left[\quad " \quad\right] + \tfrac{1}{2}g\left[\quad " \quad\right] + \tfrac{1}{2}gR$$

$$\frac{\partial S_{O_2}}{\partial x_3} = -\tfrac{1}{2}cz\left[\quad " \quad\right] + \tfrac{1}{2}cz\left[\quad " \quad\right] + \tfrac{1}{2}czR$$

$$\frac{\partial S_{O_2}}{\partial y_1} = -\tfrac{1}{2}b\left[\quad " \quad\right] + \tfrac{1}{2}b\left[\quad " \quad\right] + \tfrac{1}{2}bR$$

$$\frac{\partial S_{O_2}}{\partial y_2} = -\tfrac{1}{2}h\left[\quad " \quad\right] + \tfrac{1}{2}h\left[\quad " \quad\right] + \tfrac{1}{2}hR$$

$$\frac{\partial S_{O_2}}{\partial y_3} = -cz\left[\quad " \quad\right] + cz\left[\quad " \quad\right] + czR$$

$$\frac{\partial S_{O_2}}{\partial z} = \left[\tfrac{1}{2}c(1-x_3) + c(1-y_3) - 2c\right]\left[S_{oo_2} + \phi_1\right]$$

$$-\left[\quad " \quad\right]\left[R \log \frac{e'}{m'} P + R\right]$$

From the composition of the intermediate mixture we have the following energy expression:

$$U = ax_1\left[u_{CO_2} - u_{CO} - \tfrac{1}{2}u_{O_2}\right] + by_1\left[u_{H_2O} - u_{H_2} - \tfrac{1}{2}u_{O_2}\right]$$
$$+ gx_2\left[u_{CO_2} - u_{CO} - \tfrac{1}{2}u_{O_2}\right] + hy_2\left[u_{H_2O} - u_{H_2} - \tfrac{1}{2}u_{O_2}\right]$$
$$+ az\left[u_{CO} + 2u_{H_2} - u_{CH_4} - \tfrac{1}{2}u_{O_2}\right]$$
$$+ czx_3\left[u_{CO_2} - u_{CO} - \tfrac{1}{2}u_{O_2}\right] + 2czy_3\left[u_{H_2O} - u_{H_2} - \tfrac{1}{2}u_{O_2}\right]$$
$$+ cu_{CH_4} + (a+g)u_{CO} + (b+h)u_{H_2} + \left[e + \tfrac{1}{2}(g+h)\right]u_{O_2} + fu_{N_2}$$

$$u_{CO_2} - u_{CO} - \tfrac{1}{2}u_{O_2} = -H_{v\,CO}$$

$$u_{H_2O} - u_{H_2} - \tfrac{1}{2}u_{O_2} = -H_{v\,H_2}$$

$$u_{CO} + 2u_{H_2} - u_{CH_4} - \tfrac{1}{2}u_{O_2} = -H'$$

Then

$$-\frac{\partial U}{\partial x_1} = aH_{CO} \qquad -\frac{\partial U}{\partial x_2} = gH_{CO} \qquad -\frac{\partial U}{\partial x_3} = czH_{CO} \qquad -\frac{\partial U}{\partial y_1} = bH_{H_2}$$

$$-\frac{\partial U}{\partial y_2} = hH_{H_2} \qquad -\frac{\partial U}{\partial y_3} = 2czH_{H_2} \qquad -\frac{\partial U}{\partial z} = cH' + cx_3H_{CO} + 2cy_3H_{H_2}$$

Collecting the various results we have

$$\frac{1}{aT}\left(T\frac{\partial S}{\partial x_1} - \frac{\partial U}{\partial x_1}\right) = \frac{H_{CO}}{T} + \left(\phi_2 - \frac{3}{2}\phi_1\right) - R\log\left[\frac{\frac{ax_1+gx_2+czx_3}{m'}P}{\frac{a(1-x_1)+g(1-x_2)+cz(1-x_3)}{m'}P\left(\frac{e'}{m'}P\right)^{\frac{1}{2}}}\right]$$

$$+\tfrac{1}{2}R - (s_{O_{CO}} + \tfrac{1}{2}s_{O_{O_2}} - s_{O_{CO_2}})$$

$$\frac{1}{gT}\left(T\frac{\partial S}{\partial x_2} - \frac{\partial U}{\partial x_2}\right) = \text{same expression}$$

$$\frac{1}{czT}\left(T\frac{\partial S}{\partial x_3} - \frac{\partial U}{\partial x_3}\right) = \text{same expression}$$

At equilibrium $A_1 = 0$, $A_2 = 0$, $A_3 = 0$, $x_1 = x_2 = x_3$

The three equations above result at equilibrium in

$$R\log\frac{P_{CO_2}}{P_{CO}\cdot P_{O_2}^{\frac{1}{2}}} = \frac{H_{CO}}{T} + (\phi_2 - \frac{3}{2}\phi_1) + \tfrac{1}{2}R - (s_{O_{CO}} + \tfrac{1}{2}s_{O_{O_2}} - s_{O_{CO}}) \qquad (46)$$

$$k_{CO_2} = s_{O_{CO}} + \tfrac{1}{2}s_{O_{O_2}} - s_{O_{CO_2}}$$

Similarly we get

$$R\log\frac{P_{H_2O}}{P_{H_2}\cdot P_{O_2}^{\frac{1}{2}}} = \frac{H_{H_2}}{T} + (\phi_3 - \tfrac{1}{2}\phi_1 - \phi_5) + \tfrac{1}{2}R - k_{H_2O} \qquad (47)$$

$$k_{H_2O} = s_{O_{H_2}} + \tfrac{1}{2}s_{O_{O_2}} - s_{O_{H_2O}}$$

and

$$R\log\frac{P_{CO}\cdot P_{H_2}^2}{P_{CH_4}\cdot P_{O_2}^{\frac{1}{2}}} = \frac{H'}{T} + (\tfrac{1}{2}\phi_1 + 2\phi_5 - \phi_4) - \tfrac{3}{2}R - k' \qquad (48)$$

$$k' = s_{O_{CH_4}} + \tfrac{1}{2}s_{O_{O_2}} - s_{O_{CO}} - 2s_{O_{H_2}}$$

Equation (46) plus two times equation (47) plus equation (48) gives

$$R \log_\epsilon \left[\frac{P_{CO_2} \cdot P_{H_2O}^2}{P_{CH_4} \cdot P_{O_2}^2} \right] = \frac{H_{CO} + 2H_{H_2} + H'}{T} + (\phi_2 + 2\phi_3 - 2\phi_1 - \phi_4) - k_{CH_4} \quad (49)$$

$$k_{CH_4} = s_{O_{CH_4}} + 2s_{O_{O_2}} - s_{O_{CO_2}} - 2s_{O_{H_2O}}$$

Equation (49) is the equilibrium equation for methane combustion.

X. Derivation of Energy Equation Case III.

The relation between the thermal and chemical energies of the above gas mixture is derived as follows:

The chemical energy liberated at absolute zero is

From CO	reaction	$axH_{O_{CO}}$	
" H_2	"	$byH_{O_{H_2}}$	
" CH_4	"	$czH_{O_{CH_4}}$	
" CO_2	dissociation	$-g(1-x)H_{O_{CO}}$	
" H_2O	"	$-h(1-y)H_{O_{H_2}}$	
" CO_2	"	$-cz(1-x)H_{O_{CO}}$	From CH_4 combustion
" H_2O	"	$-2cz(1-y)H_{O_{H_2}}$	From CH_4 combustion

Adding we have

$$U - U_2 = xH_{O_{CO}} \cdot (a+g+cz) + yH_{O_{H_2}} \cdot (b+h+2cz) + H_{O_{CO}} (-g - cz) + H_{O_{H_2}} (-h - 2cz) + czH_{O_{CH_4}}$$

U_2 = thermal energy of initial mixture just before ignition.

U = " " at equilibrium point.

The thermal energy of the mixture at the equilibrium point is found as follows:

$$U = \int_0^T \gamma_v \, dT = T(a+bT+fT^2)$$

The following notation will be used:

$\gamma_{v_1} = a_1 + b_1T + f_1T^2$ mean specific heat for CO, O_2, and N_2

$\gamma_{v_2} = a_2 + b_2T + f_2T^2$ " " " " CO_2

$\gamma_{v_3} = a_3 + b_3T + f_3T^2$ " " " " H_2O

$\gamma_{v_4} = a_4 + b_4T + f_4T^2$ " " " " CH_4

$\gamma_{v_5} = a_5 + b_5T + f_5T^2$ " " " " H_2

CO_2 present at equilibrium point:

$$(a+g+cz)x$$

H_2O present at equilibrium point:

$$(b+h+2cz)y$$

CH_4 present:

$$c(1-z)$$

$CO + O_2 + N_2$ present:

$$CO = (a+g+cz)(1-x)$$

$$N_2 = f$$

$$O_2 = \tfrac{1}{2}(b+h+2cz)(1-y)+\tfrac{1}{2}(a+g+cz)(1-x)+\left[e-2cz-\tfrac{1}{2}(a+b)\right]$$

$$\text{Sum} = \tfrac{1}{2}(b+h+2cz)(1-y)+\tfrac{3}{2}(a+g+cz)(1-x)+\left[e-2cz-\tfrac{1}{2}(a+b)+f\right]$$

H present at equilibrium point:

$$(b+h+2cz)(1-y)$$

Total gas present:

$$m' = m+\tfrac{1}{2}(g+h-c)-\tfrac{1}{2}(a+g+cz)x-\tfrac{1}{2}(b+h+2cz)y$$

We may write for our thermal equation:

$$\begin{vmatrix} (a+g+cz)xH_{o_{CO}} \\ +(g+h+2cz)yH_{o_{H_2}} \\ +cz(H_{o_{CH_4}}-2H_{o_{H_2}}-H_{o_{CO}}) \\ -(gH_{o_{CO}}+hH_{o_{H_2}}) \end{vmatrix} = \begin{vmatrix} +(a+g+cz)\frac{3}{2}(1-x)T(a_1+b_1T+f_1T^2) \\ +(a+g+cz)xT(a_2+b_2T+f_2T^2) \\ +(b+h+2cz)\frac{1}{2}(1-y)T(a_1+b_1T+f_1T^2) \\ +(b+h+2cz)(1-y)T(a_5+b_5T+f_5T^2) \\ +(b+h+2cz)yT(a_3+b_3T+f_3T^2) \\ +c(1-z)T(a_4+b_4T+f_4T^2) \\ +\left[e+f-2cz-\tfrac{1}{2}(a+b)\right]T(a_1+b_1T+f_1T^2)-U_2 \end{vmatrix} \quad (50)$$

Combining coefficients and transposing:

$$(a+g+cz)x\left[H_{o_{CO}}+\tfrac{3}{2}T(a_1+b_1T+f_1T^2)-T(a_2+b_2T+f_2T^2)\right]$$
$$+(b+h+2cz)y\left[H_{o_{H_2}}+\tfrac{1}{2}T(a_1+b_1T+f_1T^2)+T(a_5+b_5T+f_5T^2)-T(a_3+b_3T+f_3T^2)\right] \quad (50\ a)$$
$$=c(1-z)T(a_4+b_4T+f_4T^2)+\left[e+f+a+\tfrac{1}{2}(5g+h+cz)\right]T(a_1+b_1T+f_1T^2)$$
$$+(b+h+2cz)T(a_5+b_5T+f_5T^2)+(gH_{o_{CO}}+hH_{o_{H_2}})-cz(H_{o_{CH_4}}-2H_{o_{H_2}}-H_{o_{CO}})-U_2$$

where U_2, the energy of the original mixture, is given by the following:

$$U_2=(a+e+f)T_2(a_1+b_1T_2+f_1T_2^2)+bT_2(a_5+b_5T_2+f_5T_2^2)$$
$$cT_2(a_4+b_4T_2+f_4T_2^2)+gT_2(a_2+b_2T_2+f_2T_2^2)+hT_2(a_3+b_3T_2+f_3T_2^2)$$

The following are expressions for the partial pressures of the various constituents and the equilibrium constants:

$$P_{CO_2}=\frac{(a+g+cz)x}{m'}P \qquad P_{H_2O}=\frac{(b+h+2cz)y}{m'}P \qquad P_{CH_4}=\frac{c(1-z)}{m'}P$$

$$P_{CO}=\frac{(a+g+cz)(1-x)}{m'}P \qquad P_{H_2}=\frac{(b+h+2cz)(1-y)}{m'}P \qquad P_{N_2}=\frac{f}{m'}P$$

$$P_{O_2}=\frac{e+\frac{1}{2}(a+g+cz)(1-x)+\frac{1}{2}(b+h+2cz)(1-y)-\frac{1}{2}(a+b+4cz)}{m'}P=\frac{e'}{m'}P$$

$$\frac{P_{CO_2}}{P_{CO}\cdot P_{O_2}^{\frac{1}{2}}}=\frac{x}{1-x}\left(\frac{m'}{e'}\frac{1}{P}\right)^{\frac{1}{2}}=K_{P_{CO_2}} \qquad \frac{P_{H_2O}}{P_{H_2}\cdot P_{O_2}^{\frac{1}{2}}}=\frac{y}{1-y}\left(\frac{m'}{e'}\frac{1}{P}\right)^{\frac{1}{2}}=K_{P_{H_2O}}$$

$$\frac{P_{CO_2}\cdot P_{H_2O}^2}{P_{CH_4}\cdot P_{O_2}^2}=\frac{(a+g+cz)x\,(b+h+2cz)^2y^2}{c(1-z)\cdot(e')^2}=K_{P_{CH_4}}$$

XI. Reduction of Equations and Method of Solution Case III.

Equations (46), (47), (49) and (50) are the four equations whose simultaneous solution gives the values of x, y, z, and T at the equilibrium point.

Substituting the numerical values of the specific heat constants and expressing H_v in terms of H_o and T according to equation (26) we have

$$4.571 \log_{10} K_{P_{CO_2}} = \frac{121250}{T} - 5.3881 \log_{10} T + 1.3335 \cdot 10^{-3} T - 0.08 \cdot 10^{-6} T^2 - 13.1 \quad (51)$$

$$4.571 \log_{10} K_{P_{H_2O}} = \frac{102100}{T} - 6.2621 \log_{10} T + 0.2361 \cdot 10^{-3} T + 0.0333 \cdot 10^{-6} T^2 + 1.1 \quad (52)$$

$$4.571 \log_{10} K_{P_{CH_4}} = \frac{347020}{T} + 5.6183 \log_{10} T - 0.0552 \cdot 10^{-3} T - 0.0133 \cdot 10^{-6} T^2 - 22.4 \quad (53)$$

$$(a+g+cz)x\left[\frac{121250}{T} + 1.34 - 1.3333 \cdot 10^{-3} T + 0.16 \cdot 10^{-6} T^2\right]$$
$$+ (b+h+2cz)y\left[\frac{102100}{T} + 1.72 - 0.2361 \cdot 10^{-3} T - 0.067 \cdot 10^{-6} T^2\right]$$
$$= c(1-z)\left[5.04 + 2.500 \cdot 10^{-3} T\right] + \left[e+f+a+\tfrac{1}{2}(3g+h+c)\right]\left[4.51 + 0.2778 \cdot 10^{-3} T\right] \quad (54)$$
$$+ \frac{121250g + 102100h + cz \cdot 21570 - U_2}{T}$$

The solution of the above four equations would be much simplified if the value of one of the variables was known. We arrive at the approximate value of z by the following method: The maximum value of z, of course, is 1. If we establish a minimum value for any given case, then the value of z is known to be between this minimum value and 1.

When z is a minimum, the partial pressure of the methane constituent at equilibrium is a maximum. From the equilibrium equation we have at any temperature T the following:

$$P_{CH_4} = \frac{P_{CO_2} \cdot P_{H_2O}^2}{P_{O_2}^2} \left(K_{P_{CH_4}}\right)^{-1}$$

If we consider that there is no dissociation of the CO_2 or H_2O; that is, $x = 1$, and $y = 1$, then the partial pressures of these two constituents will be a maximum. Also, the O_2 partial pressure will be a minimum because more O_2 is required to completely burn the CO and H_2 than is the case when there is dissociation. We may further decrease the O_2 partial pressure at equilibrium by furnishing in the initial mixture only the theoretical amount of oxygen required for complete combustion. Under these conditions the right hand member of the above equation is a maximum which will make the partial pressure of the methane a maximum.

Substituting the values for the partial pressures with $x = 1$, and $y = 1$, we have, using the required oxygen, the following:

$$K_{P_{CH_4}} = \frac{(a+g+cz)(b+h+2cz)}{4c^3(1-z)^3}$$

From which

$$(1-z) = \left[\frac{(a+g+cz)(b+h+2cz)^2}{4c^3 K_p}\right]^{\frac{1}{3}}$$

By putting z 1 on the right hand side of the above equation we get an approximate value of z which is slightly smaller than the value indicated by the equation.

$$(1-z) = \left[\frac{(a+g+c)(b+h+2c)^2}{4c^3 K_p}\right]^{\frac{1}{3}} \qquad (55)$$

From equation (55) it can be seen that z will be a minimum if c is a minimum for a given value of K_p.

Of the gases used in gas engines the methane constituent is the lowest in producer gas. An average producer gas has about the following composition by volume:

CO	22 mols	a	CO_2	7 mols	g
H_2	8 "	b	N_2	61 "	f
CH_4	2 "	c			
			total	100 mols	

Substituting these values for the constants in equation (55) we have

$$(1-z) = \left[\frac{(31)(12)^2}{32\ K_p}\right] \qquad (56)$$

From equation (53), $\log K_{P_{CH_4}} = 13.4113$ at 5500°F. absolute, a liberal maximum temperature. For lower temperatures K_P increases.

Solving (56) we get as a minimum value

$$z = 1 - \frac{1}{5690} = 0.99982$$

We can therefore take $z = 1$ without introducing error.

Putting $z = 1$ and substituting

$$\left(\frac{m'}{P}\right)^{\frac{1}{2}} = \left(\frac{mT_2}{P_2 T}\right)^{\frac{1}{2}} \qquad (57)$$

in equations (51) and (52) we have

$$4.571 \log_{10}\left[\frac{x}{1-x}\left(\frac{m}{e+\frac{1}{2}(g+h-c)-\frac{1}{2}[(a+g+c)x+(b+h+c2)y}\right)^{\frac{1}{2}}\right]$$
$$= \frac{121250}{T} - 5.3881\cdot\log_{10}T + 1.3335\cdot10^{-3}T - 0.08\cdot10^{-6}T^2 - 13.1$$
$$+ \frac{4.571}{2}\left[\log_{10}T + \log_{10}P_2 - \log_{10}T_2\right] \qquad (58)$$

$$4.571 \log_{10}\left[\frac{y}{1-y}\left(\frac{m}{e+\frac{1}{2}(g+h-c)-\frac{1}{2}[(a+g+c)x+(b+h+2c)y]}\right)^{\frac{1}{2}}\right]$$
$$= \frac{102100}{T} - 6.2631\cdot\log_{10}T + 0.2361\cdot10^{-3}T + 0.0333\cdot10^{-6}T^2 + 1.1$$
$$+ \frac{4.571}{2}\left[\log_{10}T + \log_{10}P_2 - \log_{10}T_2\right] \qquad (59)$$

Subtracting (58) from (59) we have

$$4.571 \log_{10}\left[\frac{y(1-x)}{x(1-y)}\right] = \frac{-19150}{T} - 0.8750\cdot\log_{10}T - 1.0970\cdot10^{-3}T$$
$$+ 0.1133\cdot10^{-6}T^2 + 14.2 \qquad (60)$$

The following notation is introduced:

$L = (a+g+c)$ $\qquad$ $n = (b+h+2c)$

$r = e+\frac{1}{2}(g+h-c)$ $\qquad$ $s = e+f+a+\frac{1}{2}(3g+h+c)$

$$f_c(T) = \frac{121250}{T} - 5.3881 \cdot \log_{10} T + 1.3333 \cdot 10^{-3} T - 0.08 \cdot 10^{-6} T^2 - 13.1$$

$$f_H(T) = \frac{102100}{T} - 6.2631 \cdot \log_{10} T + 0.2361 \cdot 10^{-3} T + 0.0333 \cdot 10^{-6} T^2 + 1.1$$

$$f_G(T) = \frac{-19150}{T} - 0.8750 \cdot \log_{10} T - 1.0972 \cdot 10^{-3} T + 0.1133 \cdot 10^{-6} T^2 + 14.20$$

$$f_1(T) = \frac{121250}{T} + 1.34 - 1.3333 \cdot 10^{-3} T + 0.16 \cdot 10^{-6} T^2$$

$$f_2(T) = \frac{102100}{T} + 1.72 - 0.2361 \cdot 10^{-3} T - 0.067 \cdot 10^{-6} T^2$$

$$f_3(T) = 4.51 + 0.2778 \cdot 10^{-3} T$$

$$f_4(T) = \frac{121250g + 102100h + 21570c - U_2}{T}$$

From (60) we get, using notation given above:

$$\frac{y(1-x)}{x(1-y)} = \log^{-1}\left[\frac{f_6(T)}{4.571}\right] = G$$

For any given temperature G is fully determined.

$$y = \frac{Gx}{x(G-1)+1} \qquad (61)$$

Substituting (61) in (58) we have

$$\log_{10}\left[\frac{x}{1-x}\,\frac{1}{\left[r-\frac{1}{2}\left(Lx+\frac{nGx}{x(G-1)\,1}\right)\right]^{\frac{1}{2}}}\right] = \frac{f_6(T)}{4.571} + \frac{1}{2}\log T + \frac{1}{2}\log\frac{P_2}{T_2 m} \qquad (62)$$

Substituting equation (61) in (54) with z 1, we have the following, using the new notation:

$$x^2\left[(G-1)L\ f_1(T)\right] + x\left[L \cdot f_1(T) - (G-1)\left[s \cdot f_3(T) + f_4(T)\right] + nG \cdot f_2(T)\right]$$
$$-\left[s \cdot f_3(T) + f_4(T)\right] = 0 \qquad (63)$$

To solve equations (62) and (63) proceed as follows:

In equation (62) assume a probable value of T somewhere in the neighborhood of the expected result. The right hand member of the equation and the value of G are then determined.

Solve for x by trial. Plot the curve of (62) with x and T as coordinates.

In equation (63) assume values of T which then reduces the equation to a quadratic in x which can be solved by the quadratic formula. Then plot equation (63) with (62). The intersection of the two curves gives x and T of the solution. y is then found from equation (61).

To determine the maximum explosion pressure we have

$$P = \frac{P_2 m' T}{m_2 T_2} \qquad (64)$$

XII. Numerical Example Case III.

A gas engine uses a gas having the following analysis by volume: CO 40%, H_2 20%, CH_4 10%, CO_2 8%, H_2O 2%, N_2 20%. The theoretical amount of air is supplied. Assume 10% of the products of combustion left in the clearance space. Initial pressure and temperature of charge in cylinder 14.7 lb.per.sq. in. absolute and 190°F. Compression pressure 150 lb.per. sq.in.absolute. Find the maximum temperature and pressure and the extent of combustion in the adiabatic Otto cycle.

The gas mixture in the cylinder at the end of the suction stroke consists of the initial gas plus the required air plus 10% of the products of combustion. The charge in the cylinder has the following composition:

	Mols			Mols	
CO	4.00	a	H_2O	0.62	h
H_2	2.00	b	O_2	5.00	e
CH_4	1.00	c	N_2	23.10	f
CO_2	1.38	g			

Total number of mols = 37.10 = m.

The constants for the adiabatic compression equation are

$$a_m = 34.10 \cdot 4.51 + 4.04 + 1.38 \cdot 5.42 + 0.62 \cdot 5.04 = 168.435$$

$$2b_m = (32.10 \cdot 0.5556 + 2.0 \cdot 0.5 + 5.0 + 1.38 \cdot 3.5 + 0.62 \cdot 1.25) 10^{-3}$$

$$= 29.440 \cdot 10^{-3}$$

$$\tfrac{3}{2} f_m = \tfrac{1}{2}(-1.38 \cdot 0.48 + 0.62 \cdot 0.2) 10^{-6}$$

$$\tfrac{3}{2} f_m = -0.2692 \cdot 10^{-6}$$

$$mAR = 37.10 \cdot 1.985 = 73.643$$

$$a_m + mAR = 242.078$$

Substituting the numerical values for the constants, equation (14) reduces to the following:

$$\log_{10} T_2 + \left[\bar{5}.72277\right] T - \left[\bar{10}.68390\right] T_2^2 = 3.15392$$

(Brackets indicate logarithm of the coefficient.)

By trial substitution, $T_2 = 1230^{\circ}$F abs.

The constants for the energy equation are as follows:

$$L = 6.38; \quad n = 4.62; \quad r = 5.50; \quad s = 34.98; \quad U_2 = 234{,}252;$$

$$f_4(T) = \frac{17945}{T}$$

Substituting these constants in equation (63) we have

$$x^2 \left[6.38(G-1) f_1(T)\right] + x\left[6.38\, f_1(T) - (G-1)\left(34.98\, f_3(T) + \frac{17945}{T}\right) + 4.62\, G\, f_2(T)\right] - \left[34.98 \cdot f_3(T) + \frac{17945}{T}\right] = 0 \qquad (E)$$

We have the following values for the various functions of T in equation (63) according to definitions given on page 40.

T	4700	4800	4900	5000	5100
Log G	0.9320	0.9479	0.9646	0.9804	0.9965
G	8.551	8.870	9.217	9.559	9.920
$f_1(T)$	24.411	23.891	23.398	22.928	22.481
$f_2(T)$	22.041	21.527	21.030	20.547	20.082
$f_3(T)$	5.816	5.844	5.871	5.899	5.927
$f_4(T)$	3.818	3.738	3.662	3.589	3.519

For T 5000 equation (E) reduces to

$$x^2 - 0.5935x - 0.1677 = 0$$

By quadratic formula $x = 0.802$

We have from equation (E) the following pairs of values:

T	4700	4800	4900	5000	5100
x	0.707	0.738	0.770	0.802	0.835

For the second relation between x and T we have equation (62) which reduces to the following upon the substitution of the proper constants:

$$\log_{10}\left[\frac{x}{1-x}\left[\frac{1}{5.50-3.19x-\frac{2.31Gx}{x(G-1)\ 1}}\right]^{\frac{1}{2}}\right] = \frac{f_c(T)}{4.571} + \tfrac{1}{2}\log T - 0.16241 \quad (F)$$

For T = 5000 the value of the right hand member of equation (F) is 0.78662

Solution by trial gives $x = 0.800$

Similarly we get from equation (F) the following pairs of values:

T	4900	5000	5100
x	0.849	0.827	0.802

The intersection of the graphs of equation (E) and equation (F), fig.6, page 44, gives:

$T = 5050^\circ F$ abs. $x = 0.816$

For T = 5050, G = 9.751

Then equation (61) gives

$y = 0.977$

Equation (64) gives

$$P = \frac{150 \cdot 32.73 \cdot 5050}{37.10 \cdot 1230} = 543.3 \text{ lb.per.sq.in.absolute}$$

Fig 6 Case III

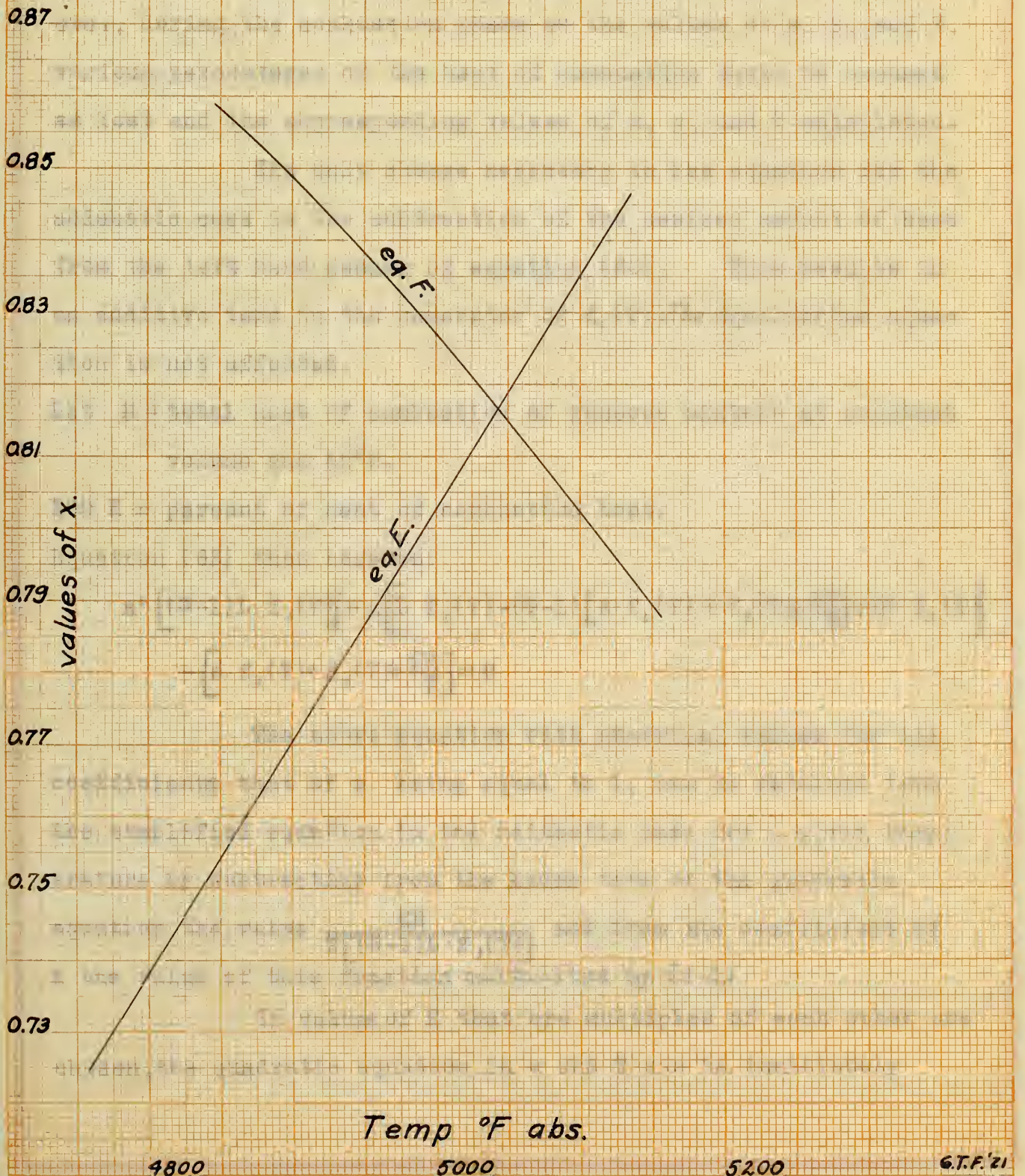


Fig 6 Case III
Temp °F obs.
Activity to x_{Ni}
0.87
0.85
0.83
0.81
0.79
0.77
0.75
0.73

XIII. Effect of Loss of Heat During Combustion on the Maximum Temperature and Pressure and the Extent of Combustion in Case III.

To show the loss of heat by radiation, conduction, etc., during the combustion phase on the values of x, y, and T, various percentages of the heat of combustion shall be assumed as lost and the corresponding values of x, y, and T calculated.

The only change necessary in the equation for the adiabatic case is the subtraction of the desired amount of heat from the left hand member of equation (50). This results in an additive term in the numerator of $f_4(T)$. The equilibrium equation is not affected.

Let H = total heat of combustion of gaseous mixture at constant volume and 62°F.

100 K = percent of heat of combustion lost.

Equation (63) then becomes:

$$x^2\left[(G-1)L\ f_1(T)\right]+x\left[L\ f_1(T)-(G-1)\left[s\cdot f_3(T)+f_4(T)+\frac{KH}{T}\right]+nG\cdot f_2(T)\right]$$
$$-\left[s\ f_3(T)+f_4(T)+\frac{KH}{T}\right]=0$$

The above equation with numerical values for the coefficients, that of x being equal to 1, can be obtained from the simplified equation in the adiabatic case for a given temperature by subtracting from the known term of the quadratic equation the value $\frac{KH}{T\left[(G-1)L\cdot f_1(T)\right]}$ and from the coefficient of x the value of this fraction multiplied by (G-1)

If values of K that are multiples of each other are chosen, the quadratic equation in x and T can be immediately

written down from the equation of the adiabatic case after the correction terms have been calculated for the first value of K.

The following values of K are therefore chosen:

Case No.	0	1	2	3	4
K%	0	2.5	5.0	7.5	10.0

H 1,038,070 from analysis, page 41, and heating values given in Appendix B.

For 5000° and Case 1:

$$\left[\frac{KH}{T\cdot(G-1)L\cdot f,(T)}\right] = \frac{0.025\cdot 1038070}{5000\cdot 8.559\cdot 6.38\cdot 22.928} = 0.00415$$

$$\left[\quad "\quad\right](G-1) = 8.559\cdot 0.00415 = 0.0355$$

For Case 0:

$$x^2 - 0.5935x - 0.1677 = 0$$

For Case 1:

$$x^2 - 0.6290x - 0.1718 = 0$$

For Case 2:

$$x^2 - 0.6645x - 0.1760 = 0$$

For Case 3:

$$x^2 - 0.7000x - 0.1801 = 0$$

For Case 4:

$$x^2 - 0.7355x - 0.1843 = 0$$

For the other temperatures we deduce similar sets of equations.

Solutions of the various quadratic equations give the following table of values for x:

T	4700	4800	4900	5000	5100
Case No. 0	0.707	0.738	0.770	0.802	0.835
Case No. 1	0.738	0.770	0.802	0.835	0.868
Case No. 2	0.772	0.802	0.834	0.867	0.901
Case No. 3	0.802	0.834	0.866	0.900	0.934
Case No. 4	0.833	0.866	0.899	0.933	0.967

The following pairs of values satisfy the equilibrium equation (F), page 43:

T	4000	4300	4600	4900	5000	5100
x	0.970	0.945	0.905	0.849	0.827	0.802

Plotting the above values we have the chart, fig. 7, shown on page (48). The lines for heat losses from 15% to 30% were obtained by extrapolation.

The following values of x and T are obtained from the chart. The values of y are then calculated by means of equation 61 and values of P from equation 64.

% loss of heat:	0	5	10	15	20	25	30
T °F.abs.	5050	4930	4810	4680	4550	4410	4260
x	0.816	0.843	0.868	0.892	0.913	0.932	0.949
y	0.977	0.980	0.983	0.986	0.988	0.990	0.993
P#/sq.in.abs.	543	529	516	500	485	468	452

The curves on page 49 give a graphical representation of the data given in the above table. From this curve sheet it can be seen that x and y increase with heat lost during the explosion phase while T and P decrease.

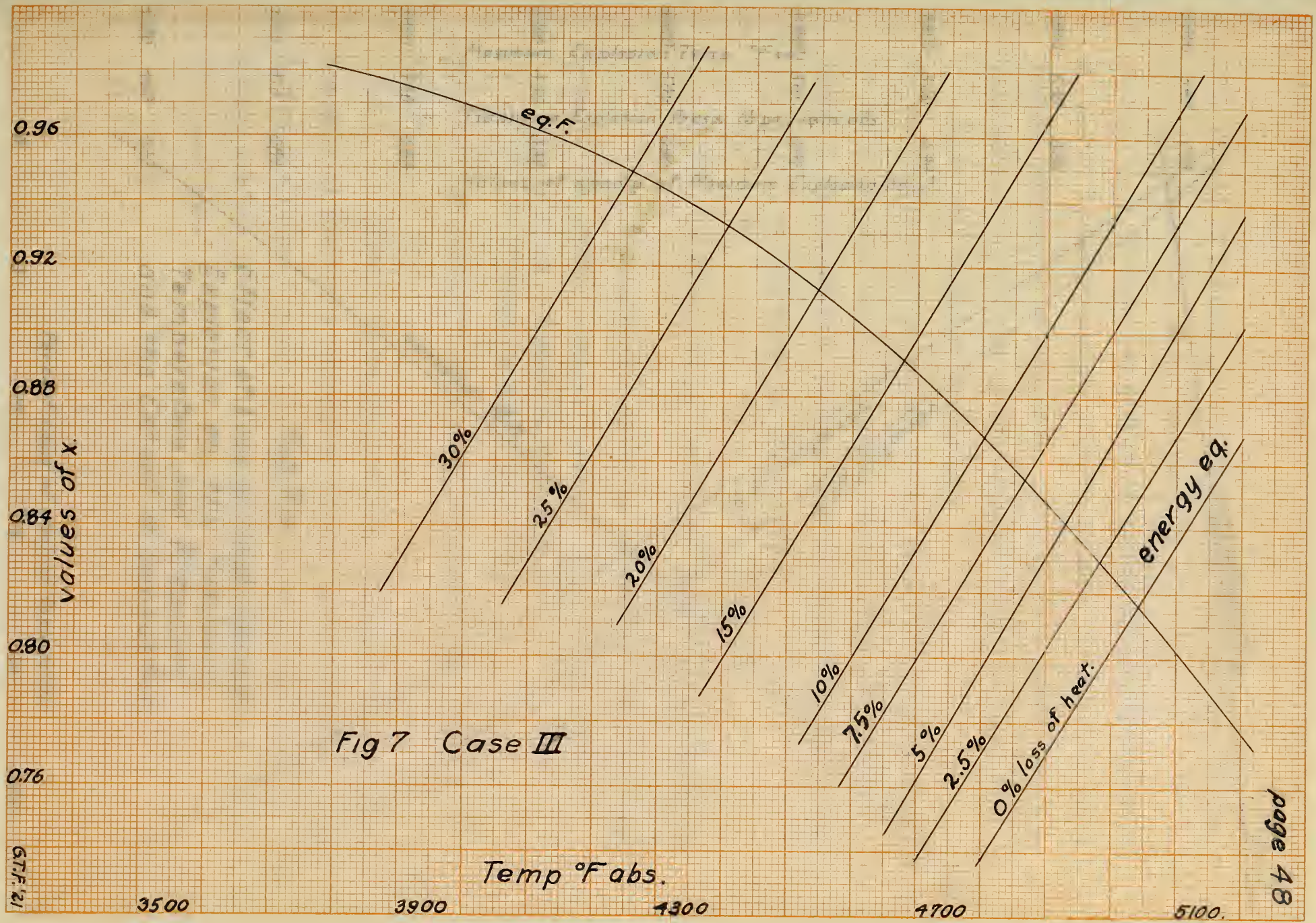


Fig 7 Case III

GT.F. 121

Fig 1 Case II
Temp. of Air.
Altitudes in Feet
Distance in Miles
Curve of Pressure
5% 2% 1% 10% 12% 50% 52% 30%

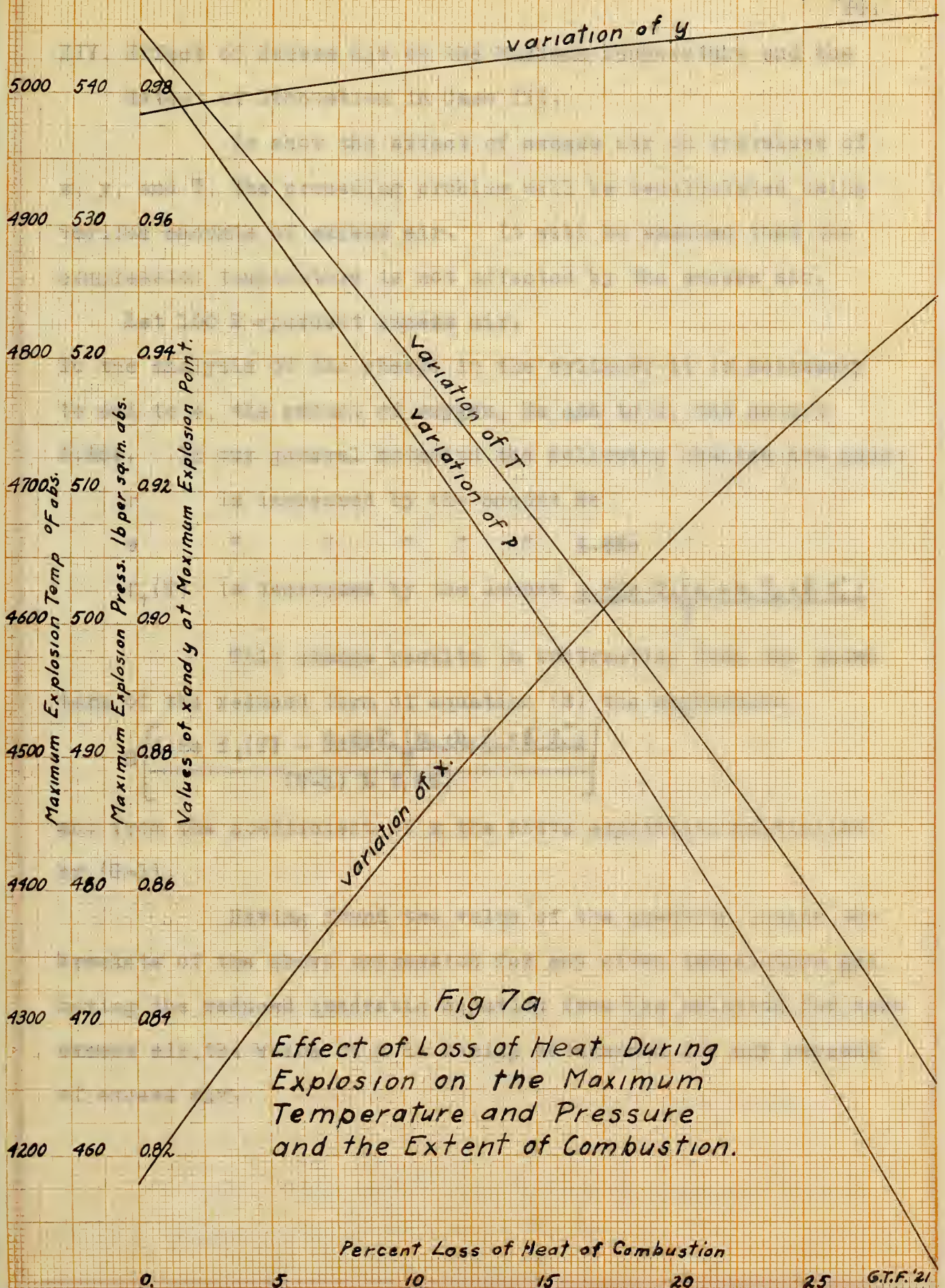


Fig 7a

Effect of Loss of Heat During Explosion on the Maximum Temperature and Pressure and the Extent of Combustion.

Variation of γ

Variation of T

Variation of P

Percent Loss of Heat of Combustion

Maximum Temperature of Explosion	Maximum Pressure of Explosion	Ratio of Specific Heats γ
5000	510	0.28
4800	520	0.294
4600	500	0.30
4500	490	0.308
4400	480	0.316
4300	470	0.324
4200	460	0.332

Fig 7a

Effect of Loss of Heat During Explosion on the Maximum Temperature and Pressure and the Extent of Combustion.

XIV. Effect of Excess Air on the Maximum Temperature and the Extent of Combustion in Case III.

To show the effect of excess air on the values of x, y, and T, the preceding problem will be recalculated using various amounts of excess air. It will be assumed that the compression temperature is not affected by the excess air.

Let 100 E = percent excess air.

To the analysis of the charge in the cylinder it is necessary to add to e, the amount of oxygen, Ee and to f, the amount 3.8Ee. In our general notation the following changes are made:

r is increased by the amount Ee

s " " " " " 4.8Ee

$f_1(T)$ is decreased by the amount $\frac{4.8Ee\ T_2(a_1+b_1T_2+f_1T_2^2)}{T}$

This change results in subtracting from the known term of the reduced form of equation (E) the expression

$$E\left[\frac{4.8e\ f_3(T) - \frac{4.8eT_2(a_1+b_1T_2+f_1T_2^2)}{T}}{(G-1)\ L\ f_1(T)}\right]$$

and from the coefficient of x the above expression multiplied by (G-1).

Having found the value of the quantity inside the brackets of the above expression for any given temperature and having the reduced quadratic equation from the solution for zero excess air, the value of x is easily determined for any percent of excess air.

We have from the solutions the following values of x:

Temp. °F absolute	Percent excess air 0	10	20	30	40
4600	0.678	0.682	0.689	0.694	0.700
4800	0.738	0.803	0.867	0.935	1.002
5000	0.802	0.873	0.945	1.017	1.090

The only change in the equilibrium equation (62) as given on page 43 is the addition of the quantity Ee to r. Making this change the following values are calculated:

Temp. °F absolute	Percent excess air 0	10	20	30	40
4300	0.945	0.968	0.977	0.981	0.983
4600	0.905	0.934	0.948	0.955	0.960
4900	0.849	0.881	0.900	0.912	0.921
5100	0.802	0.835	0.856	0.872	0.883

Plotting the values given in the above tables we have the chart, fig. 8, on page 52, from which the following solutions are obtained:

% excess air	0	10	20	30	40
T °F abs.	5050	4975	4890	4790	4680
x	0.816	0.865	0.902	0.930	0.952
y	0.977	0.984	0.989	0.992	0.993
P#/sq.in.abs.	543	537	530	522	512

The values of y are calculated from equation (61) and the values of P from equation (64) as before.

The above table is presented in graphical form on page 53, fig. 8 a.

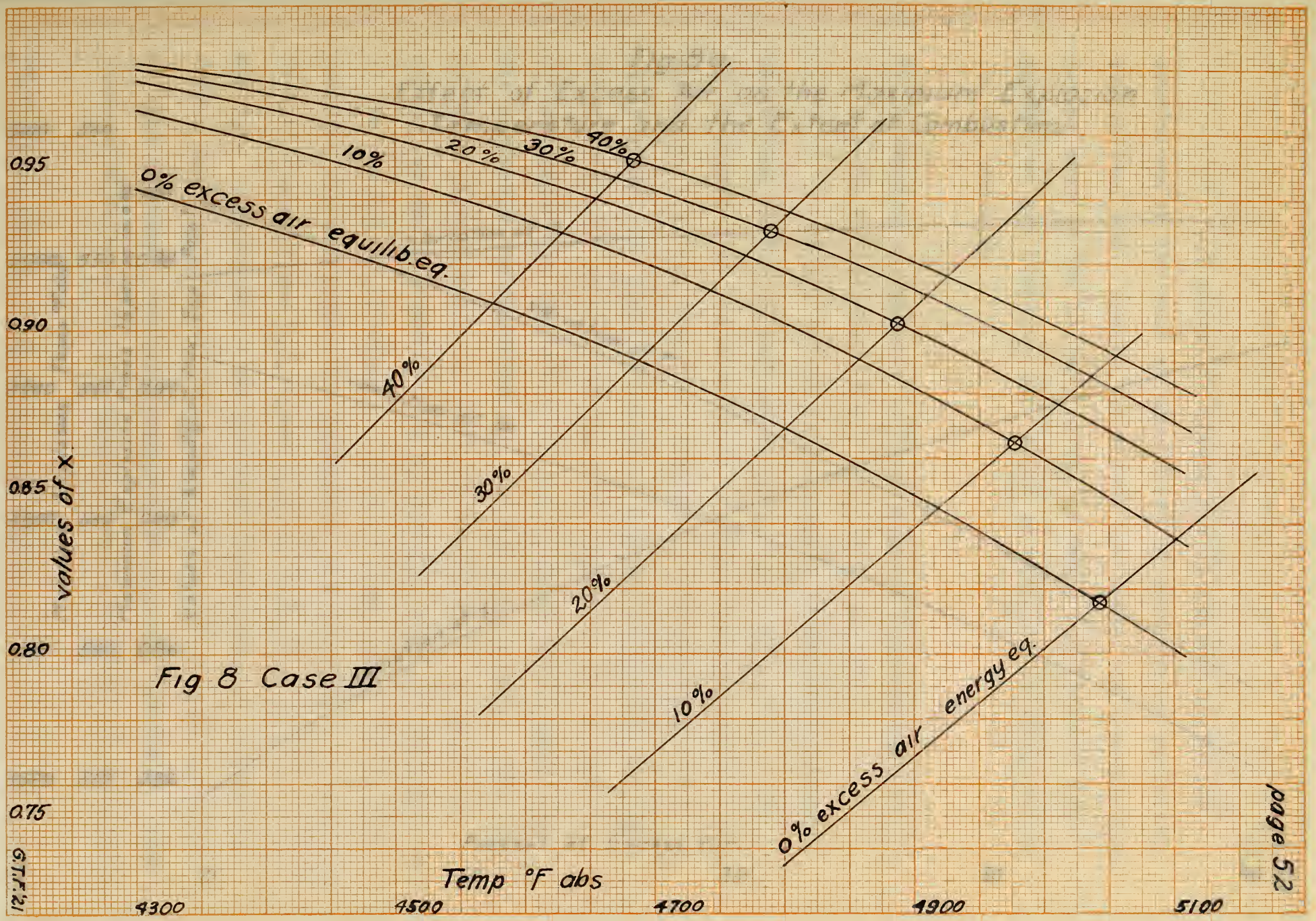


Fig 8 Case III

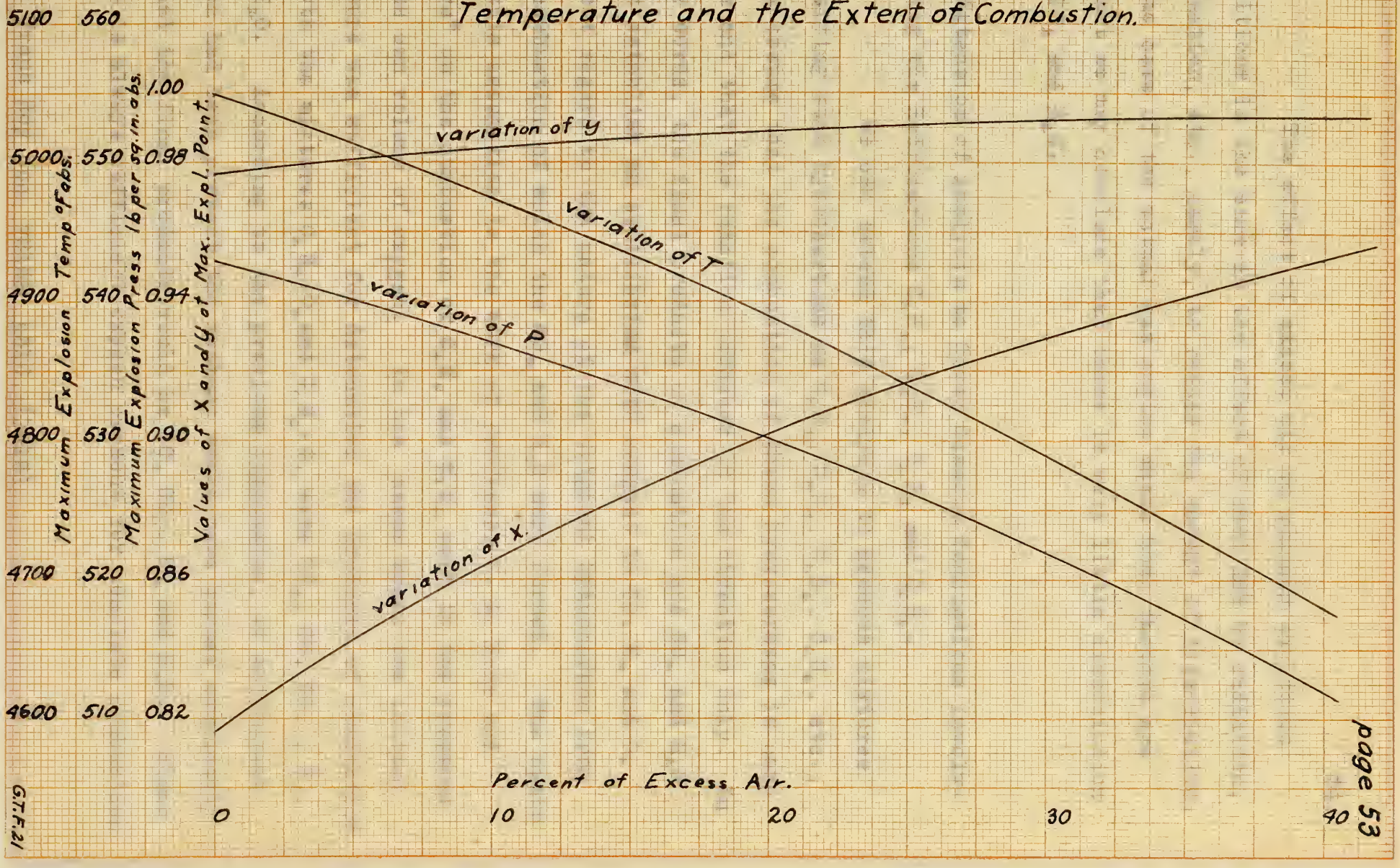
page 52

G.T.F.'21

Fig 8 Case III
% excess air supplied
100%
50%
25%
10%
0% excess air supplied
Height in feet
x % solvent

Fig 8a

Effect of Excess Air on the Maximum Explosion Temperature and the Extent of Combustion.



G.T.F.12

Maximum Explosion Temp. at Exit
Maximum Explosion Press. Input Pressure
Volume of Explosive at Max. Expl. Temp.
Explosive Mixture
Explosive Mixture
Explosive Mixture

The effect of excess air on maximum explosion conditions is the same as the effect of heat lost by radiation, conduction, etc., namely, to reduce the amount of dissociation. In the case of the actual gas engine where both factors are present we may conclude that there is very little dissociation of CO_2 and H_2O.

XV. Extension of Analysis to Cover Gaseous Combustions Involving the Hydrocarbons C_2H_2, C_2H_4, C_2H_6 and C_6H_6.

We can extend this analysis to gaseous mixtures containing such hydrocarbons as C_2H_2, C_2H_4, C_2H_6, C_6H_6, etc., if we assume that the combustion of these hydrocarbons is complete and that the reaction proceeds in one direction only. In other words, the final products of combustion are CO_2 and H_2O which establish an equilibrium with respect to CO, H_2 and O_2 without regard to the nature of the original hydrocarbon from the combustion of which the CO_2 and H_2O were formed. The basis for this assumption is the work of Professor W. A. Bone and others* on the combustion of C_2H_4 and C_2H_6 each in the presence of its own volume of oxygen. In the cases where the initial pressure was sufficient for detonation the products of combustion of both the mixtures $C_2H_4+O_2$ and $C_2H_6+O_2$ were CH_4, CO, CO_2, H_2, and H_2O. According to the previous discussion, if sufficient oxygen had been present the methane would have burned completely so that the final products would be CO, CO_2, H_2 and H_2O. Since there is always sufficient oxygen present for complete combustion

*Phil Trans Roy Soc v215A p310 (1915)

in gas engine mixtures, we may accept the assumption of the complete combustion of the hydrocarbons as being very close to the truth in gas engine explosions.

It has been shown previously (page 6) that lack of specific heat data at high temperatures for the hydrocarbons introduces no serious serror in the calculation of the compression temperature. We are not concerned with the specific heat data of the hydrocarbons above the compression temperature because in the energy equation we consider the thermal energy of the final products which with the above assumption will not contain any hydrocarbons and the thermal energy of the initial mixture which is at the compression temperature. With the assumption of the complete combustion of the hydrocarbons the conditions at the maximum explosion point of any gaseous mixture ordinarily met in practise can be calculated by the methods of the preceding pages.

APPENDIX A

SPECIFIC HEATS

Appendix A

Specific Heats

The following is from manuscript by Prof. G. A. Goodenough, and gives specific heat equations for N_2, O_2, CO, air, H_2O, CO_2 and CH_4.

"In the analysis of the processes occurring in the internal combustion engine an accurate knowledge of the specific heats of the various components of the gas mixture is of first importance. The specific heats are required (1) in the determination of the variation of the heat of combustion of a fuel with the temperature; (2) in the calculation of the temperature attained when the fuel mixture is burned; (3) in the establishment of the equilibrium equations for the various reactions that receive consideration.

At the present time it cannot be said that our knowledge of the specific heats of gases, especially at very high temperatures, is satisfactory. The results obtained from experiments are discordant. Any expression for the specific heat of a gas must be regarded as conjectured and subject to change as more reliable experimental data are obtained.

Experimental methods: Two principal methods have been used in the determination of the specific heats of gases. (1) The constant pressure method in which the gas under constant atmospheric pressure is made to flow through a heater and then through a calorimeter where it is cooled. A comparison

of the temperature change with the heat rejected gives the specific heat. This method was used by Regnault and subsequently by Joly, Holborn and Henning, and others. It is applicable at moderate temperatures. (2) The explosion method used by Langen and by Pier. A combustible mixture of gases in a closed vessel is ignited and the rise of pressure is determined. The change of temperature is calculated from the pressures, and assuming that the chemical energy of the original mixture is all transformed into thermal energy, the mean specific heat of the gas mixture for the temperature range involved is readily computed. The explosion method is the only one applicable at very high temperatures.

A comparison of the results obtained from the two methods shows that the explosion experiments give specific heat values somewhat higher than those obtained from the constant pressure experiments.

A critical discussion of experimental methods and results may be found in the Report of the British Association Committee on Gaseous Explosions. This is published in Clerks "Gas, Petrol, and Oil Engines," Vol.1.

The Diatomic Gases. Experiments on the diatomic gases as nitrogen, oxygen, CO, and air, appear to establish two facts.

1. The specific heat is a linear function of the temperature.
2. The specific heat per mol is nearly the same for all these gases.

The equations representing the experiments of Langen, Pier, and Holborn and Henning are respectively,

Langen $\gamma_{p_m} = 6.8 + 0.0006t$

Pier $\gamma_{p_m} = 6.9 + 0.00045t$

Holborn and Henning $\gamma_{p_m} = 6.58 + 0.000532t$

In these expressions t denotes the temperature on the C scale, and γ_{p_m} denotes the mean specific heat from 0°- $t^\circ C$. Expressions for the instantaneous specific heat are obtained by doubling the coefficient of t. This we obtain

$\gamma_p = 6.8 + 0.0012t$

$\gamma_p = 6.9 + 0.0009t$

$\gamma_p = 6.58 + 0.001064t$

Lewis and Randall* propose as a compromise the formula

$\gamma_p = 6.50 + 0.0010T$

in which T denotes absolute temperatures on the C. scale.

The preceeding formulas apply to all the common diatomic gases except hydrogen. For hydrogen Pier gives the mean specific heat

$\gamma_{p_m} = 6.7 + 0.00045t$

whence

$\gamma_p = 6.7 + 0.0009t$

That is, Pier makes the variation with temperatures the same as for the other gases, but takes 6.7 instead of 6.9 for the absolute term. Lewis and Randall propose for the specific heat of hydrogen the equation

$\gamma_p = 6.5 + 0.0009t$

*Jour Am Chem Soc vol 34, 1912

which agrees quite closely with Pier's equation.

The formulas of Lewis and Randall may be accepted as a fair compromise of the conflicting experimental data. To transform the formulas to the F.scale we multiply the coefficients of T by 5/9. If we let $T/1000 = \theta$, in which T denotes absolute temperatures on the F.scale the formulas become:

For N_2, O_2, CO and air, $\gamma_p = 6.5 + 5/9\ \theta$ (1)

For H_2 $\gamma_p = 6.5 + \frac{1}{2}\ \theta$ (2)

Carbon Dioxide: The experiments on the specific heat of carbon dioxide may be classified as follows:

1. The earlier experiments of Regnault and Wiedemann at low temperatures. These have been supplemented by the experiments of Joly and Swann also at low temperatures.

2. The experiments of Holborn and Austin extending to about 800° C and the later experiments of Holborn and Henning which covered the range 0° to 1400° C.

3. The explosion experiments: Of these the experiments of Mallard and Le Chatelier may be left out of consideration as the results are obviously inexact. Langen and Pier have also used the explosion method; the latter's experiments extending to 2100° C. There is little doubt that Pier's results should be given considerable weight.

The following are some of the formulas that have been proposed. In these γ_{pm} denotes th mean specific heat per mol between 0° C and t° C.

Holborn and Austin,

$$\gamma_{P_m} = 8.923 + 3.045 \cdot 10^{-3} t - 0.735 \cdot 10^{-6} t^2$$

Holborn and Henning,

$$\gamma_{P_m} = 8.84 + 3.257 \cdot 10^{-3} t - 0.792 \cdot 10^{-6} t^2$$

Langen,

$$\gamma_{P_m} = 8.7 + 0.0026 t$$

Pier,

$$\gamma_{P_m} = 8.79 + 3.3 \cdot 10^{-3} t - 0.95 \cdot 10^{-6} t^2 + 0.1 \cdot 10^{-9} t^3$$

Lewis and Randall have proposed the following formula based on Pier's results at high temperatures and Holborn and Henning's results at the lower temperatures:

$$\gamma_P = 7.0 + 7.1 \cdot 10^{-3} T - 1.86 \cdot 10^{-6} T^2$$

In this formula T denotes absolute temperature on the C scale and γ_P is the instantaneous specific heat per mol.

A comparison of some of the proposed equations is shown in fig. 9, page 61. The points of temperatures 500-2000° are obtained from Holborn and Austin's formula, the points for the higher temperatures from Pier's formula. It will be observed that at the lower temperatures the increase of specific heat with the temperature is quite marked, but at the higher temperature the rate of increase becomes smaller. This decrease in the slope of the C_p curve is clearly indicated by the experiments of Holborn and Austin, and Holborn and Henning; and the indication is strengthened by Pier's experiments, which give points on a curve continuous with the Holborn and Austin curve. Langen's formula represented by the straight line gives reasonable values up to 2000° but for higher temperatures cannot be

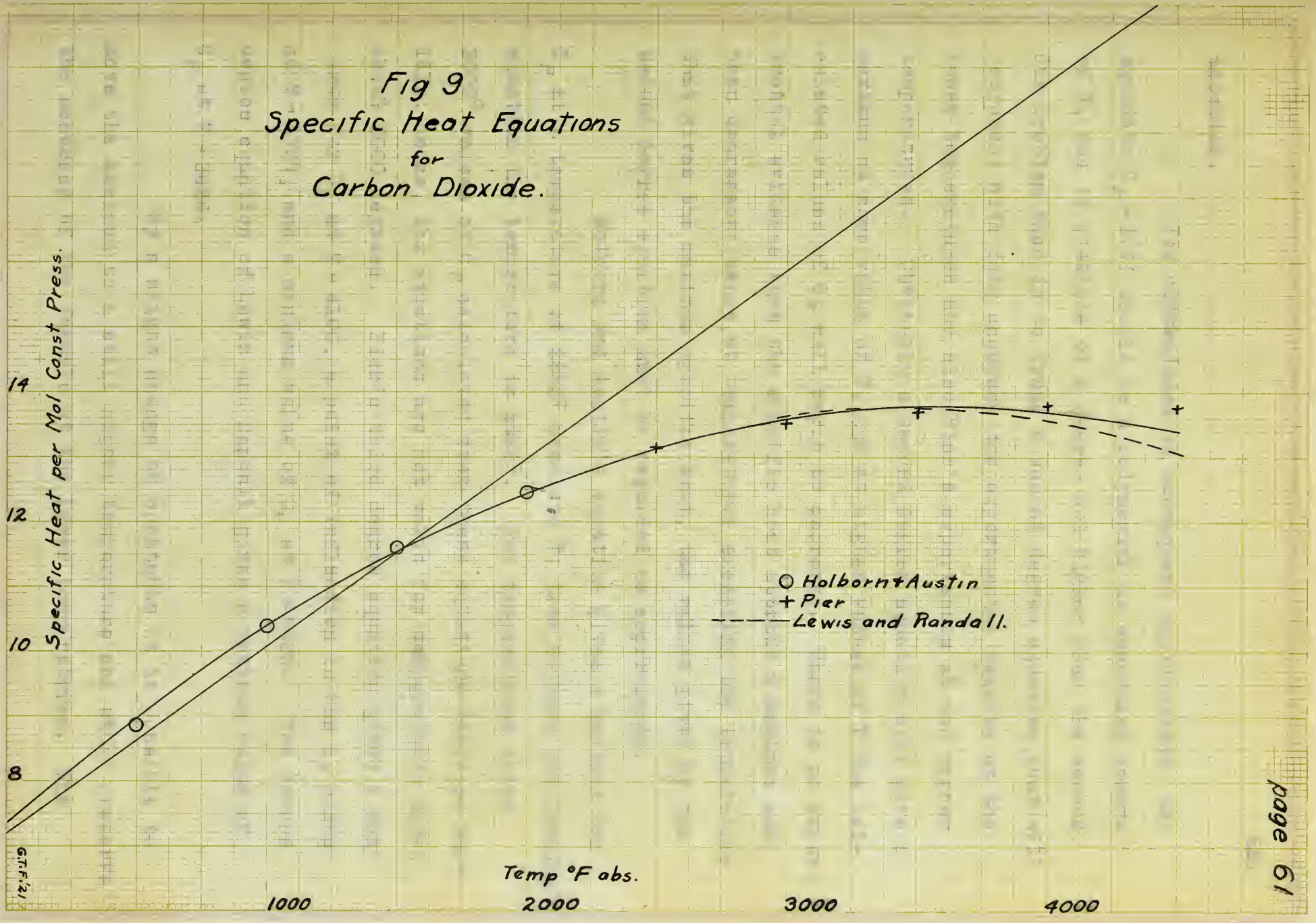


Fig 9
Specific Heat Equations
for
Carbon Dioxide.
Specific Heat per Mol Const Press.
14
12
10
8
Temp °F abs.
1000
2000
3000
4000
O Holborn+Austin
+ Pier
Lewis and Randall.
G.T.F.'21

Carbon Dioxide
Specific Heat Equations
Fig 2
Specific Heat per Mol const press.
Temp in deg. Kelvin
1000
2000
3000
4000
Temp in deg Rankine
+ Hirn
O Holborn & Austin

accepted.

For convenience in subsequent applications, the equation $C_p = f(T)$ should be a polynomial in ascending powers of T, and if possible of a degree not higher than the second. Our problem then is to frame a second degree equation that will represent with fair accuracy the experimental results at the lower temperatures and also Pier's experiments at the higher temperatures. Obviously a second degree equation will give a maximum at some value of T, and at higher values of T the calculated values of C_p will begin to decrease. There is no experimental evidence that the specific heat attains a maximum and then decreases; hence, at temperatures exceeding the temperature that gives the maximum specific heat, the values given by the second degree equation must be regarded as approximate.

Holborn and Austin's equation gives a maximum for C_p at a temperature of 2883° absolute F; from Holborn and Henning's equation the temperature is 2982°. For temperatures above 3000° values of C_p calculated from these equations decrease rapidly; hence, the equations are not valid for temperatures above about 3000 degrees. Pier's third degree equation gives a maximum for C_p at $T = 4100$, a point of inflection in the C_p curve at $T = 4767$, and a minimum value of C_p at $T = 5433$. The second degree equation of Lewis and Randall gives a maximum value of C_p at $T = 3436$.

By a slight change of constants it is possible to move the maximum to a still higher temperature and still preserve the accuracy of the formula at the lower temperatures. The

equation finally developed is

$$\gamma_p = 7.41 + 3.5\ \theta - 0.48\ \theta^2 \qquad (A)$$

in which, as usual, $\theta = T/1000$. The value of θ for a maximum γ_p is

$$\theta = 3.5/2\times 0.48 = 3.648 \quad \text{or} \quad T = 3648 \text{ degrees absolute F.}$$

The graphical representation of this equation is shown by the full line curve of fig.9,p.61.The dash line curve represents the equation of Lewis and Randall. The agreement between the proposed equation and the experimental values is shown in the following tables:

Mean specific heat per lb. between	Observed		Calculated Holborn & Austin	Calculated Equation (A)
20° - 200°C	0.2168	Regnault	0.2173	0.2180
20° - 440°C	0.2306	H. and A.	0.2312	0.2310
20° - 630°C	0.2423	" "	0.2410	0.2403
20° - 800°C	0.2486	" "	0.2486	0.2479

Joly found for the mean specific heat between 10° - 100°C the value 0.2120. The equation gives 0.2116.

Values of the instantaneous specific heats per pound at the lower temperatures:

Temp.°C.	Regnault	Wiedemann	Langan	Holborn &Austin	Holborn &Henning	Equation (A)
0	0.1870	0.1952	0.1980	0.2028	0.2009	0.2049
100	0.2145	0.2169	0.2100	0.2161	0.2152	0.2169
200	0.2396	0.2387	0.2220	0.2285	0.2289	0.2282
400	-----	------	0.2450	0.2502	0.2517	0.2488
600	-----	------	0.2690	0.2678	0.2706	0.2665
800	-----	-------	0.2920	0.2815	0.2829	0.2814

Pier obtained the mean specific heat at constant volume from 0° - t°C for five temperatures. The results are given in the following table:

Higher temperature	γ_v Observed	$\gamma_p = \gamma_v + 1.99$	Calculated Pier's formula	Equation(A)
1611	9.976	11.966	12.059	12.059
1725	10.06	12.05	12.168	12.173
1831	10.27	12.26	12.261	12.266
1839	10.28	12.27	12.274	12.273
2110	10.47	12.46	12.463	12.456

The proposed equation gives with fair accuracy the specific heats at the lower temperature and represents Pier's results with nearly the same precision as Pier's formula. Apparently the equation may be accepted with confidence up to the limit $T = 4500^{\circ}F$.

Water Vapor: It is well shown that the specific heat of water vapor near the saturation limit varies with the pressure as well as with the temperature. However at these lower temperatures the pressure of the H_2O component in a gas mixture is usually small, and some low constant pressure may be assumed. At the higher temperatures the variation of the specific heat with the pressure is negligible.

Data for the specific heat at the lower temperature are furnished by three sets of experiments.

1. The explosion experiments of Langen, from which is deduced the formula

$$\gamma_{Pm} = 7.9 + 0.00215t$$

for the mean specific heat between 0° and $t^{\circ}C$.

2. The experiments of Holborn and Henning, which are represented by $\gamma_{Pm} = 8.43 - 0.3815 \cdot 10^{-3} t + 0.792 \cdot 10^{-6} t^2$

3. The experiments of Knoblauch and Jakob; and the later experiments of Knoblauch and Mollier extending to 550° C.

The discrepancy between the experimental results is shown by the curves of fig.(10), page 66. In this figure the points marked + are obtained from Goodenough's formula* for specific heat of superheated steam taking a pressure of 1 lb. per sq.in. The straight line that represents Langen's equation runs entirely above these points, and the Holborn and Henning curve from 250 degrees C. runs far below them. That Holborn and Henning's results are low due to systematic errors in the experimental method has been asserted by Callendar and others; and it is likewise probable that Langen's straight line runs altogether too high for the lower range of temperature. The results obtained from the experiments of Knoblauch are however worthy of entire confidence.

For the higher temperatures the only reliable evidence is furnished by Pier's explosion experiments. Pier's formula for mean specific heat per mol from 0 to t degrees C is

$$\gamma_{Pm} = 8.065 + 0.5 \cdot 10^{-3} t + 0.2 \cdot 10^{-9} t^3$$

The curve that represents this formula (see fig.10) is almost coincident with the Holborn and Henning curve for temperature above 300 degrees C. At very high temperatures the third degree term in Pier's formula assumes importance and gives rise to a rate of increase of C_p with t that is scarcely credible. Curves of the instantaneous specific heat from 1000 degrees to 2750 degrees C. are shown in fig. 11, page 67. It will be seen that Pier's curve crosses Langen's straight line at t = 2050 and then rises rapidly.

*Principles of Thermodynamics, p.105. 3rd ed.

Fig 10
Specific Heat of H_2O

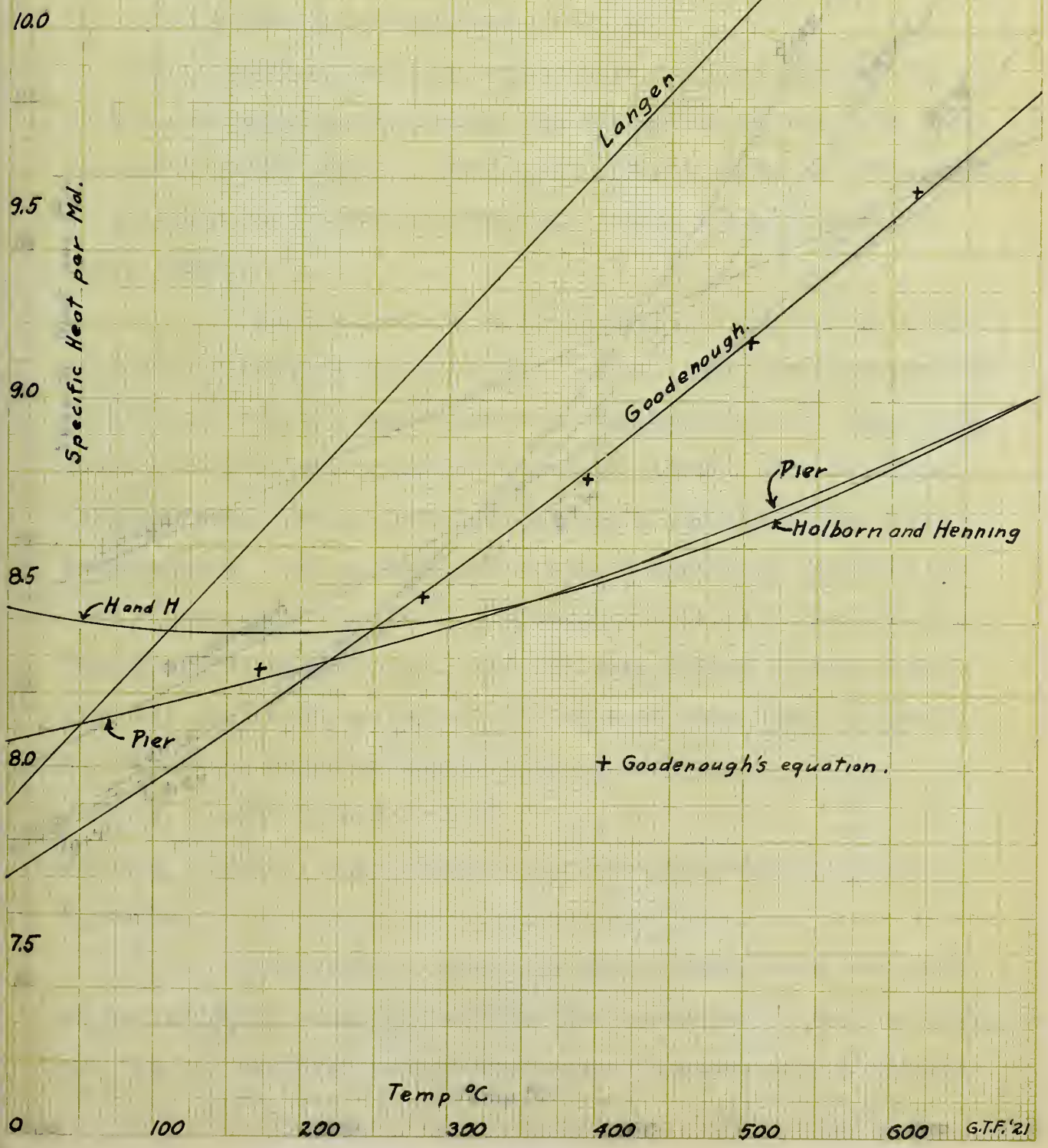
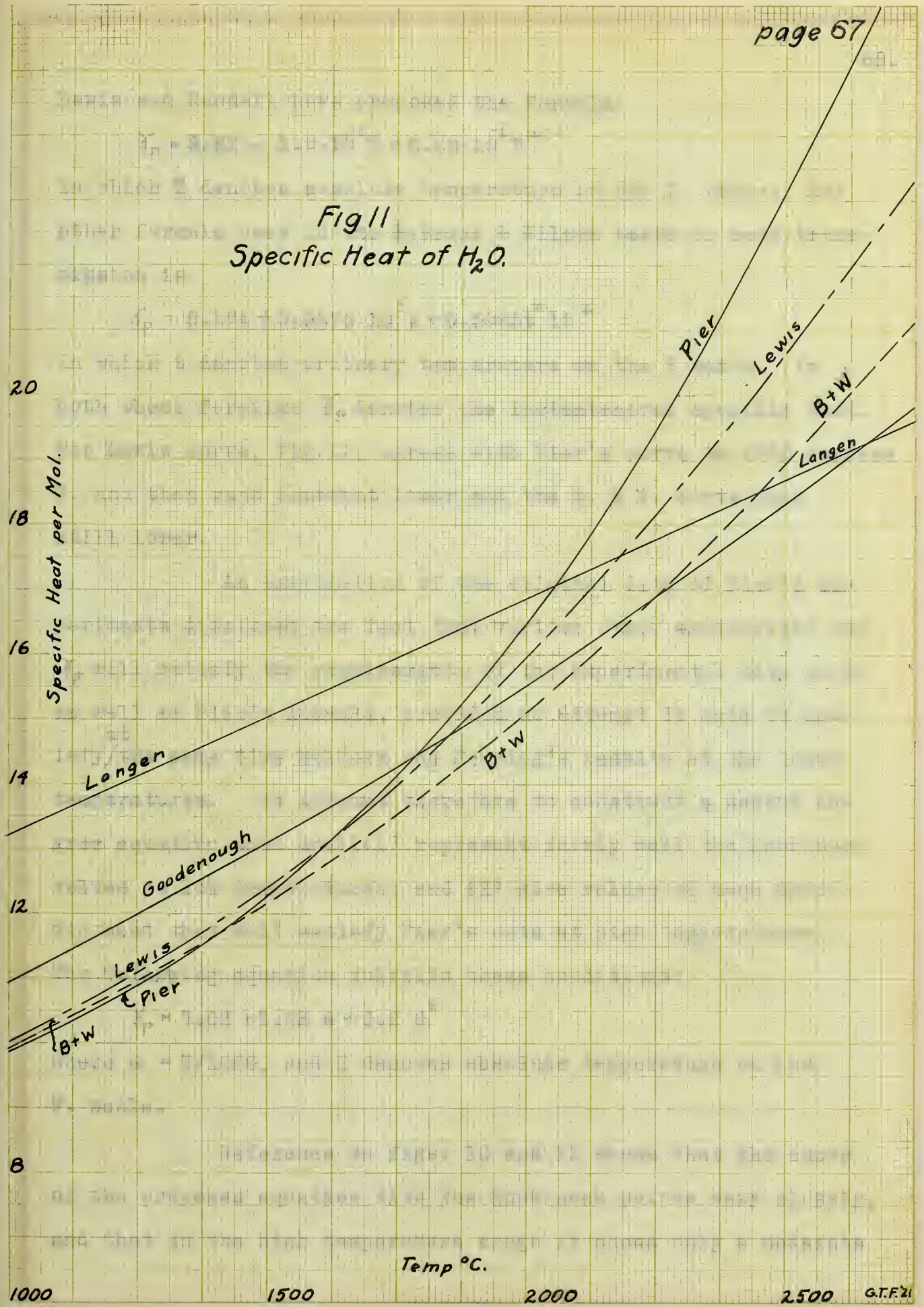


Fig 10

Specific Heat of H_2O

Fig 11

Specific Heat of H_2O.



Lewis and Randall have proposed the formula:

$$\gamma_p = 8.81 - 1.9 \cdot 10^{-3} T + 2.22 \cdot 10^{-6} T^2$$

in which T denotes absolute temperature on the C. scale. Another formula used in the Babcock & Wilcox tests on heat transmission is

$$\gamma_p = 8.174 + 0.0576 \cdot 10^{-3} t + 0.5085 t^2 \cdot 10^{-6}$$

in which t denotes ordinary temperature on the F scale. In both these formulas γ_p denotes the instantaneous specific heat. The Lewis curve, fig.11, agrees with Pier's curve to 1750 degrees C. and then runs somewhat lower and the B. & W. curve runs still lower.

An examination of the original data of Pier's experiments discloses the fact that various other expressions for γ_p will satisfy the requirements of the experimental data quite as well as Pier's formula, provided no attempt is made to satisfy at the same time Holborn and Henning's results at the lower temperatures. We attempt therefore to construct a second degree equation that shall(1) represent fairly well the Knoblauch values at low temperatures; and (2) give values of mean specific heat that will satisfy Pier's data at high temperatures. The following equation fulfills these conditions:

$$\gamma_p = 7.03 + 1.25\ \theta + 0.2\ \theta^2$$

where $\theta = T/1000$, and T denotes absolute temperature on the F. scale.

Reference to figs. 10 and 11 shows that the curve of the proposed equation fits the Knoblauch points very closely, and that in the high temperature range it shows only a moderate

rate of increase of γ_p with the temperature. The equation is a fair compromise between the high values obtained by Langen and the obviously low values of Holborn and Henning.

Methane: We have the following values for the mean specific heat of methane per mol at constant pressure for the range 18 degrees to 208 degrees C.

Regnault 9.507; Wullner 9.106; Lussana 9.483

For lower temperatures we have the recent values of Heuse:

T^oC	-80	-55	-30	5	15
γ_p	8.08	8.08	8.14	8.42	8.50

For the instantaneous specific heat we shall take the linear equation:

$$\gamma_p = 6.03 + 0.005T$$

in which T is in absolute degrees F.

The agreement with Heuse's values is as follows:

T^oF(abs)	348	392	438	501	519
Heuse	8.08	8.08	8.14	8.42	8.50
Calculated	7.77	7.99	8.22	8.53	8.62

For the range 18 degrees to 208 degrees C. or from 524 degrees to 866 degrees F. absolute, the equation gives for the mean specific heat 9.504 which agrees with Regnault and Lussana.

Data for the higher temperatures are entirely lacking. The equation chosen does not give an unreasonable rise in specific heat with temperature and when used in the equilibriu m equation for the reaction $C + 2H_2 \rightarrow CH_4$ gives an equilibrium curve

that agrees as well as could be expected with the discordant data available for the equilibrium at high temperatures. We may, therefore, accept the specific heat equation for methane given above as being the best possible in the light of the meager experimental data available."

Experimental data on the specific heat of gases other than those treated by Professor Goodenough are so meager that we are hardly justified in establishing a relation between specific heat and temperature. However, for the gases acetylene, ethylene, ethane and benzene which appear in small quantities in ordinary fuel gases, a large error in the specific heat of any one of the above gases introduces only a small error in the total specific heat of the gas and air mixture burned in the engine.

Being guided by the fact that the linear relation for the specific heat of methane produces an equilibrium equation that satisfies the high temperature data fairly well and also by the fact that the experimental data on the specific heat of benzene which is available up to 350 degrees C. is also satisfied by a linear relation we shall assume that the specific heat equations for acetylene, ethylene and ethane are also linear.

Acetylene (C_2H_2): For acetylene we have only the two points by Heuse for the instantaneous specific heat at constant pressure as follows:

t°C	T°F.abs.	γ_p
+18	524	10.43
−71	364	9.13

The straight line through these two points is given by the following relation. T is in degrees Fahrenheit absolute. $\gamma_p = 6.19 + 0.0081\ T$

Ethylene C_2H_4: For ethylene we have the identical values of Regnault and Lussana of 11.32 as the mean molecular specific heat at constant pressure for the range 10 degrees to 202 degrees C. and the following instantaneous values by Heuse:

t degrees C.	T degrees F.abs.	γ_p observed.	γ_p Calculated from eq. below
+ 18	524	10.22	10.22
- 36	427	9.17	9.57
- 68	369	8.79	9.18
- 91	256	8.64	8.41

The proposed equation for the instantaneous specific heat of ethylene at constant pressure is

$$\gamma_p = 6.67 + 0.0068T$$

with T in degrees Fahrenheit absolute. This equation gives a value of 11.31 for the mean specific heat over the range 10 degrees to 202 degrees C. as compared with the value of 11.32 given by Regnault and Lussana. The comparison with Heuse's values is given above.

Ethane: C_2H_6 - For ethane we again have only Heuse's determinations which are as follows:

t°C.	T°F.abs.	γ_p (obs.)	γ_p (calc.)
+15	518	12.40	12.29
- 35	428	11.04	11.27
- 82	344	10.44	10.32

The equation that gives the above calculated values is

$$\gamma_p = 6.43 + 0.0113T$$

Benzene Vapor, C_6H_6: For benzene vapor we have data over a wider range and can therefore place more confidence in our derived relation. The experimental data are:

Temp. range °C.	Temp. range °F(abs.)	γ_p observed.	Investigator	γ_p Calculated
34-115	553-699	23.337(mean)	Wiedemann	23.34
35-180	555-816	25.913 "	"	25.91
116-218	700-884	29.270 "	Regnault	29.27
350	1122	38.947(inst.)	Thiabaut	38.95

The proposed equation for the instantaneous specific heat of benzene vapor at constant pressure is

$$\gamma_p = 4.00 + 0.0318T$$

with T in degrees Fahr. absolute.

A comparison of the calculated and experimental results is given in the above table.

Graphical comparisons between the calculated and experimental values of specific heat for methane, acetylene, ethylene, ethane, and benzene vapor are given in the figures 12,13,14,15, and 16, on pages 73, 74, 75, 76, and 77 respectively.

In the preceding discussion on specific heats it has been assumed that the specific heats of gases are independent of pressure. While this assumption is not correct we have the following to show that in the range of temperatures existing in the gas engine the effect of pressure on specific heat is negligible.

For the more permanent gases we have as an example the specific heat equation of Plank* for nitrogen expressed as a

*Physikalische Zeit. 11-633 (1910)

Fig 12

Specific Heat of Methane CH_4

$\gamma_p = 6.03 + 0.005\,T$

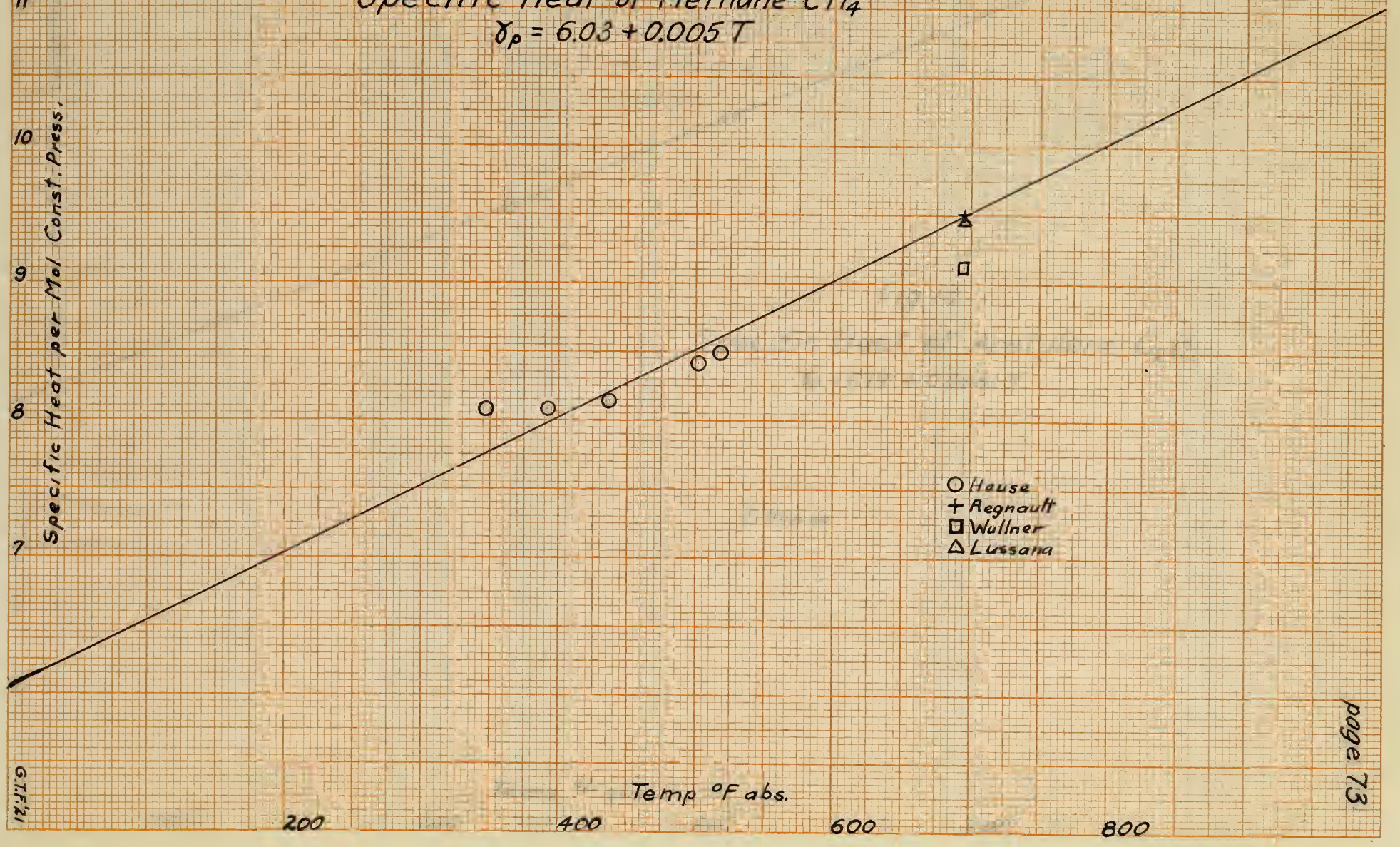


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Fig. 15

Specific Heat of Methane at Const. Pressure

$C_p = 0.503 + 0.000\,209\,T$

Temp. in deg. F.

Specific Heat per Mol Const. press.

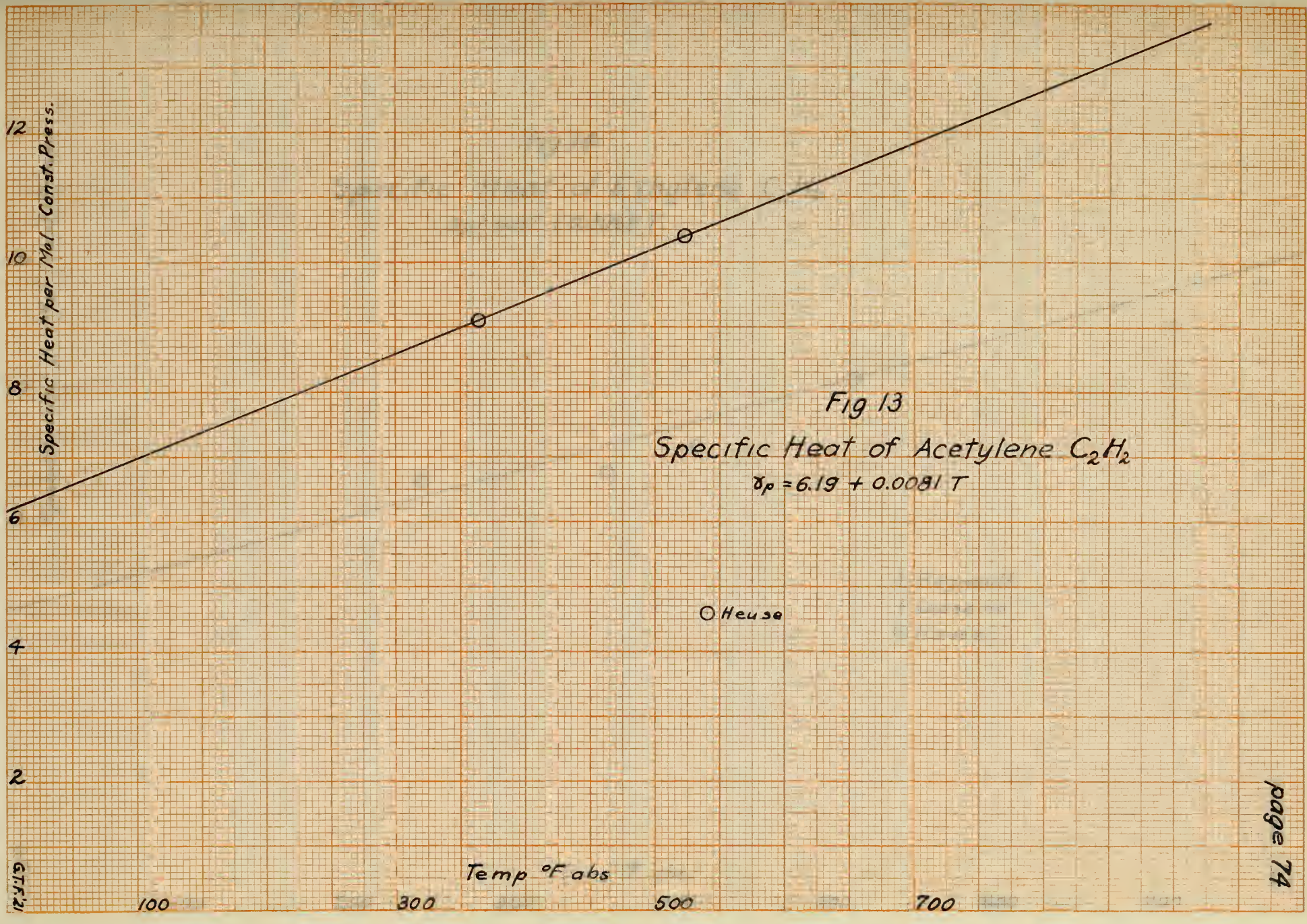

Fig 13

Specific Heat of Acetylene C_2H_2

$\gamma_p = 6.19 + 0.0081\ T$

Specific Heat of Water Cal/gm °C
Temp °C

Fig 14

Specific Heat of Ethylene C_2H_4

$\gamma_p = 6.67 + 0.0068T.$

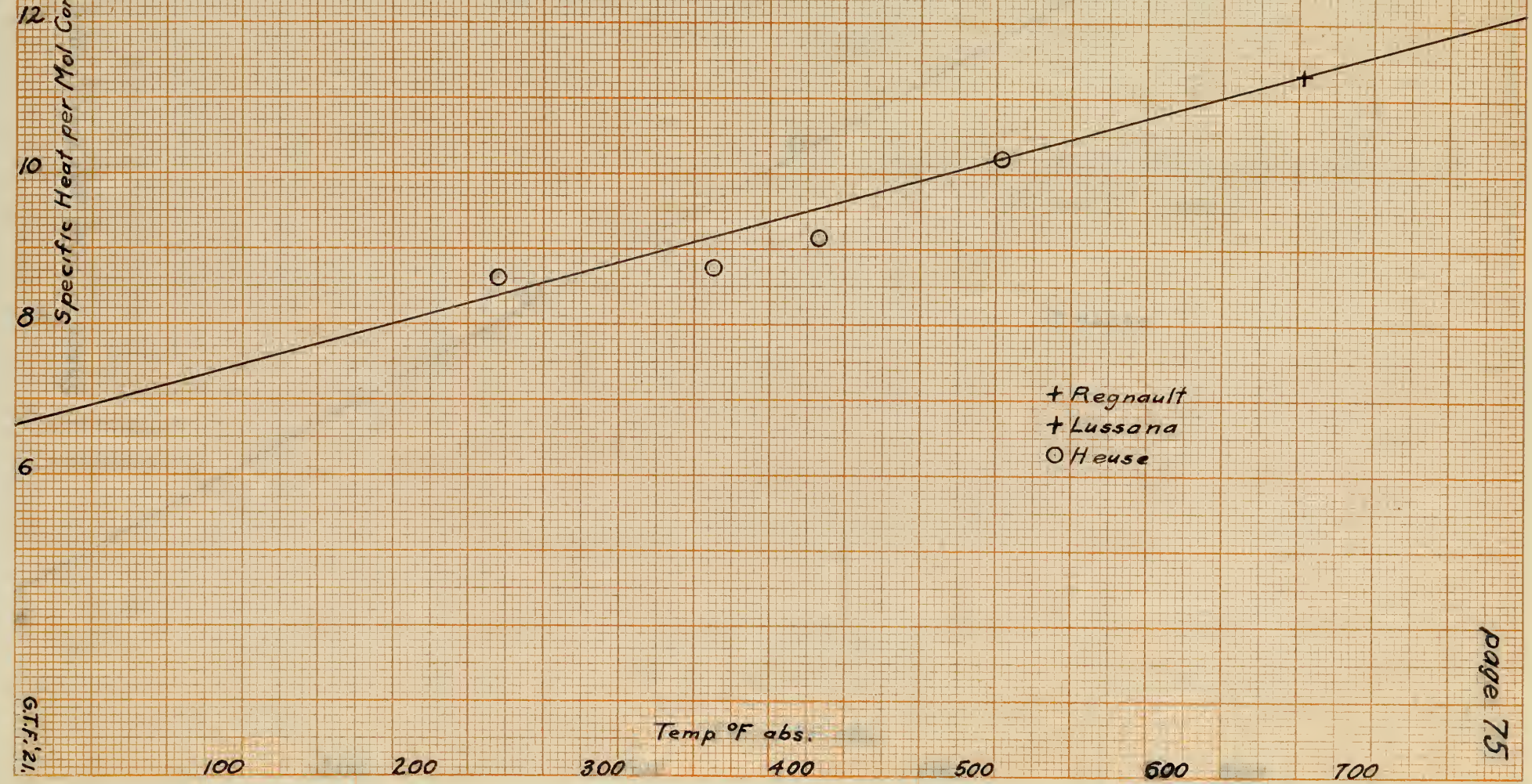

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Fig 4

Specific heat of liquids C_nH_{2n+2}

Specific heat, water unity

Temp. in degs.

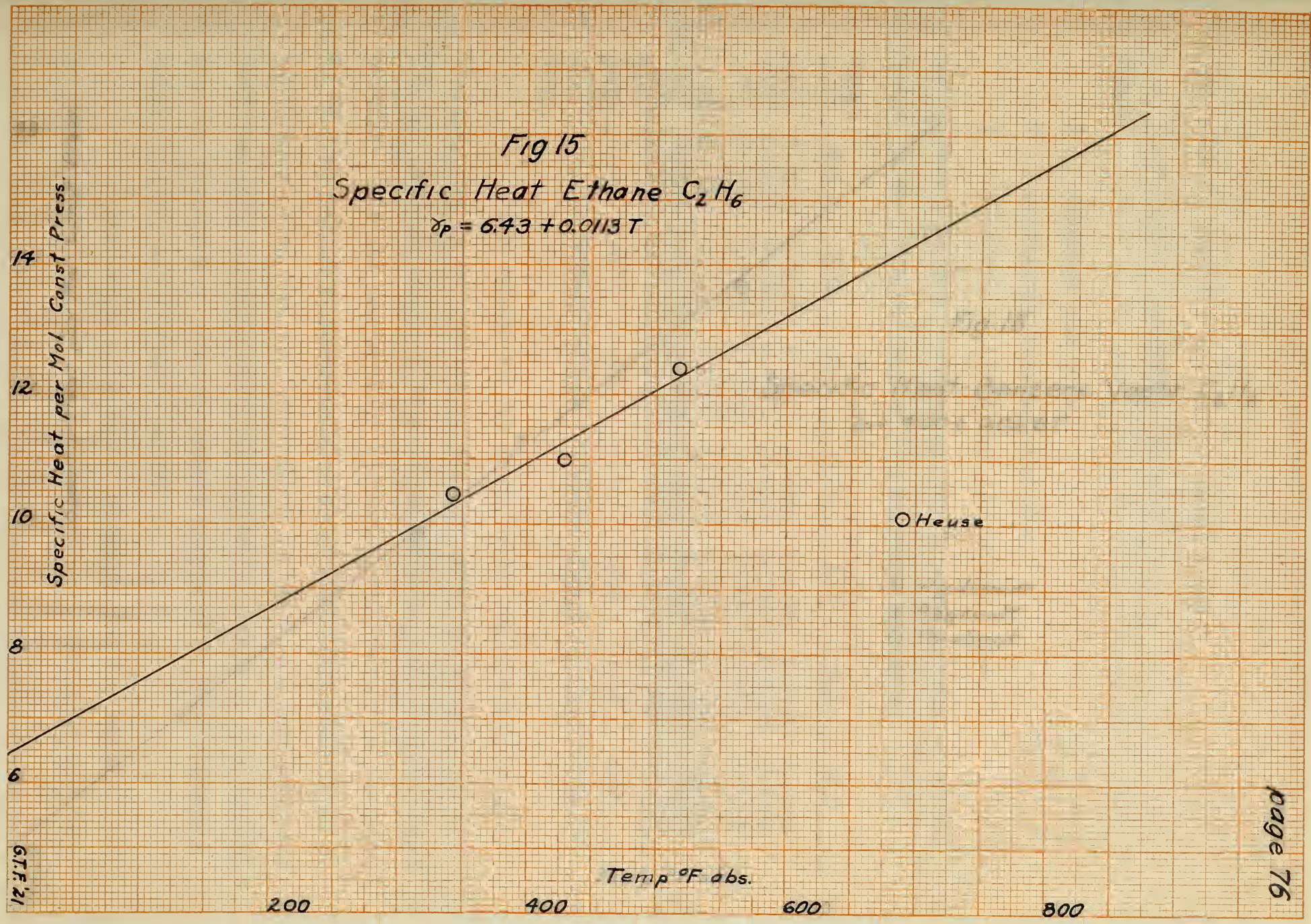


Fig 15
Specific Heat Ethane $C_2 H_6$
$\gamma_p = 6.43 + 0.0113\,T$
Specific Heat per Mol Const Press.
14
12
10
8
6
Heuse
Temp °F abs.
200
400
600
800

G.T.F. '21

Fig. 12.

Observed linear elongation of a
rod of cast iron.

$\Delta l = 2.42 + 0.0001 T$

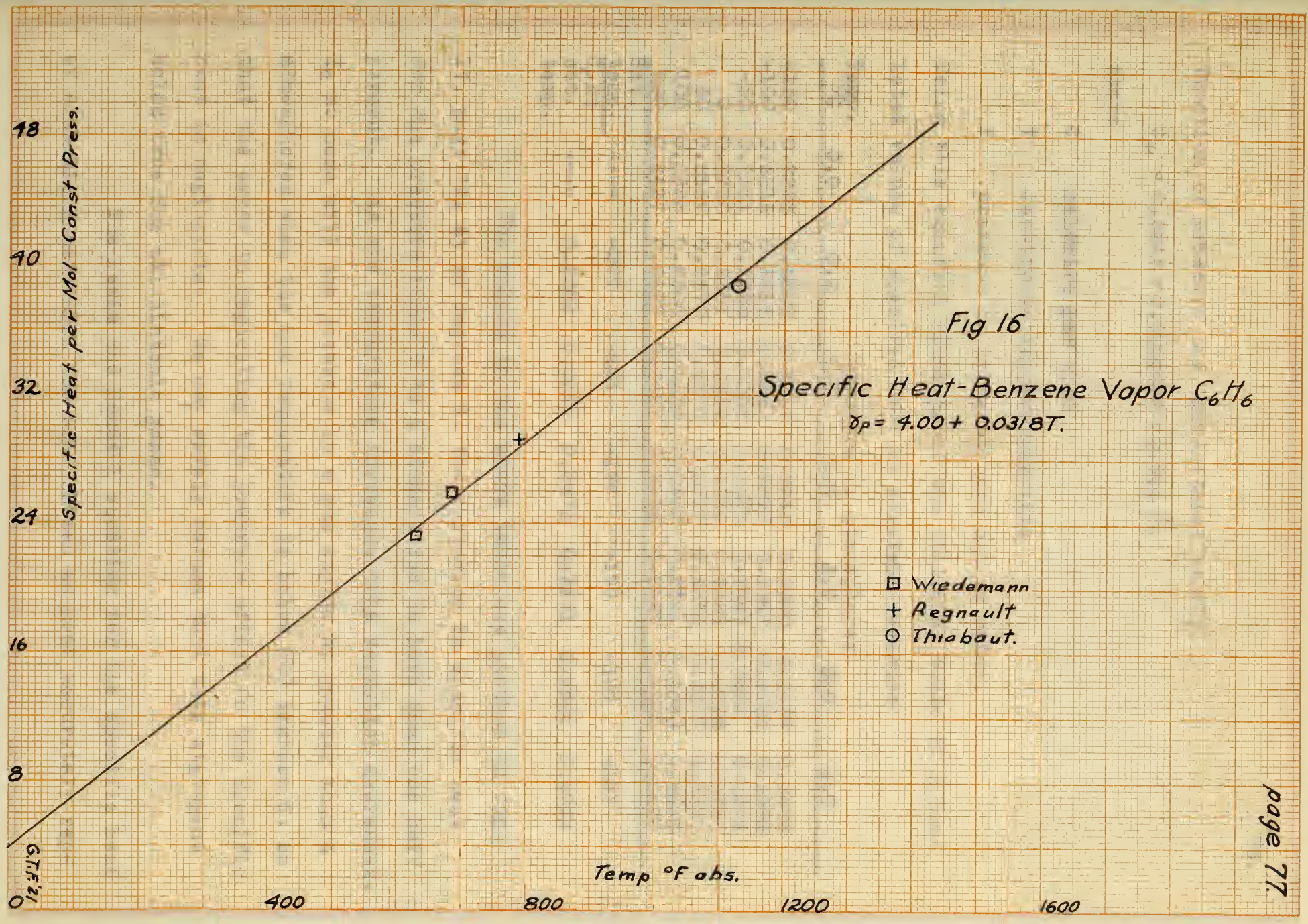


Fig 16

Specific Heat - Benzene Vapor C_6H_6

$\gamma_p = 4.00 + 0.0318T.$

G.T.F. '21

function of pressure and temperature; namely,

$$C_p = 0.2246 + 0.000038T + 0.905\frac{P}{T^3}$$

where

C calories per gram

T Centigrade degrees absolute

P pressure in kilograms per square meter.

Using this equation Plank gives the following table of calculated values of specific heat at constant pressure:

Temp. °C	Pressure in atmospheres 0.0	0.2	0.5	1.0	2.0	3.0	4.0
-150	0.2293	0.2303	0.2317	0.2342	0.2390	0.2439	0.2488
-100	0.2312	0.2316	0.2321	0.2329	0.2347	0.2364	0.2382
-50	0.2331	0.2333	0.2335	0.2339	0.2347	0.2355	0.2364
0	0.2350	0.2351	0.2352	0.2354	0.2359	0.2363	0.2368
50	0.2369	0.2370	0.2370	0.2372	0.2374	0.2377	0.2380
100	0.2388	0.2388	0.2389	0.2390	0.2391	0.2393	0.2395
200	0.2427	0.2427	0.2427	0.2428	0.2429	0.2430	0.2430
Sat. temp.	----	-207	-201	-196	-190	-185	-187
C_p at sat. temp.	----	0.2334	0.2395	0.2473	0.2591	0.2681	0.2759

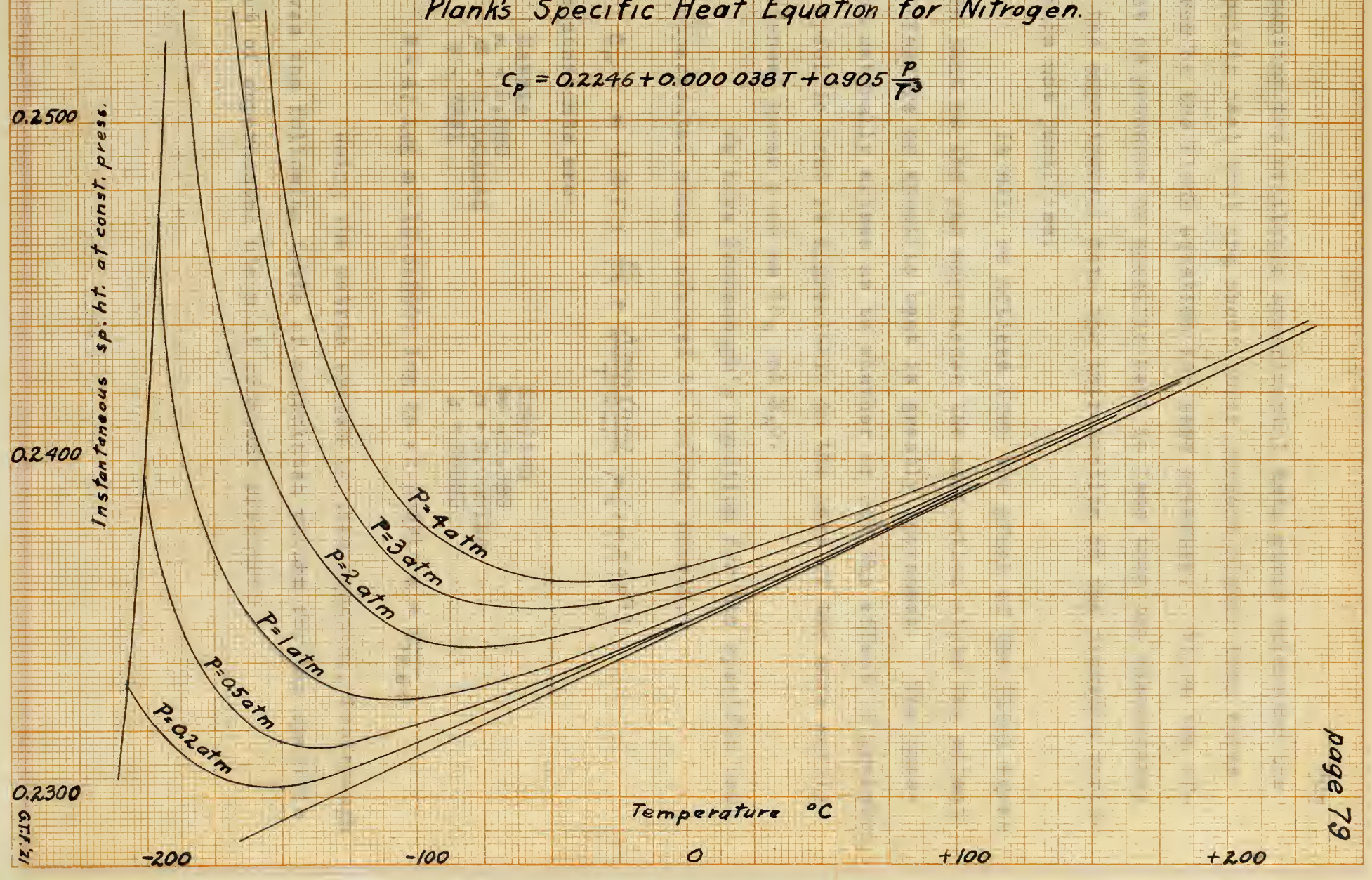
The values in the above table are plotted in fig. 17, page 79, At 50 degrees C. the variation in specific heat for the pressure range 0 to 4 atmospheres is less than one half percent. As the temperature increases this variation decreases. In no case will the pressure in a gas engine by greater than 4 atmospheres when the gas temperature is below 200 degrees C. so that the error in neglecting the pressure effect on the specific heat is negligible. We may safely assume that this statement holds true for all diatomic gases.

The Lewis and Randall equation for the specific heat of diatomic gases which has been chosen as most accurately rep-

Fig 17

Plank's Specific Heat Equation for Nitrogen.

$$C_p = 0.2246 + 0.000038T + 0.905\frac{P}{T^3}$$



G.T.F. '21

Fig. 1.

Atomic Specific Heat Equation for Nitrogen.

$C_p = 0.2482 + 0.0000 \, 0.0 \, 1 + 0.0000 \, 0.0 \, 0 \, 2 \, t^2$

Temperature C°

Instantaneous sp. ht. at const. press.

p=1 atm

p=2 atm

p=3 atm

p=4 atm

p=5 atm

p=6 atm

resenting the available experimental data gives values for the specific heat that are about three percent higher than those given by the Plank equation for zero pressure. Since the effect of pressure on specific heat is less than the discrepancy in the experimental data the introduction of the pressure variable is not justified.

It will be noticed from the graph of the Plank equation that as the gas approaches the saturation state the effect of pressure on specific heat is greatly increased. The question naturally arises as to whether or not the effect of pressure on specific heat is appreciable in the case of the more easily condensed gases such as CO_2 and H_2O.

We have Goodenough's equation for the specific heat of superheated steam referred to before; namely,

$$C_p = \alpha + \beta T + \frac{\gamma}{T^2} + \frac{A m n (n+1)}{T^{n+1}} p(1 + 2a p^{\frac{1}{2}})$$

The constants are

Metric	English
$\alpha = 0.320$	$\alpha = 0.320$
$\beta = 0.0002268$	$\beta = 0.000126$
$\gamma = 7371$	$\gamma = 23583$

$N = 4$; $\log m = 10.82500$; $\log 2a = \bar{2}.53391$; $A = \frac{1}{777.64}$

Using the metric system in this equation, Goodenough gives the following table of calculated values for the specific heat of superheated steam at constant pressure:

Temp. °C.	Pressure Kg. per sq. cm. 0	2	4	6	8
150	0.457	0.490	0.527	----	-----
200	0.460	0.479	0.498	0.522	0.545
250	0.466	0.477	0.489	0.503	0.517
300	0.473	0.480	0.487	0.496	0.504
350	0.480	0.485	0.490	0.496	0.502
400	0.489	0.492	0.496	0.500	0.504
450	0.498	0.500	0.503	0.505	0.508
500	0.508	0.509	0.511	0.513	0.515
550	0.518	0.519	0.520	0.521	0.523

1 Kg per sq. cm =14.223 lb. per sq. in.

We have the equation deduced in the first part of this discussion for the specific heat of water vapor, a function of temperature alone, as follows:

$$\gamma_p = 7.03 + 1.25 \cdot 10^{-3} T + 0.2 \cdot 10^{-6} T^2$$

Changing to the Centigrade scale we have for the specific heat per gram

$$C_p = 0.3905 + 0.125 \cdot 10^{-3} T + 0.036 \cdot 10^{-6} T^2$$

From this equation we have the following calculated values:

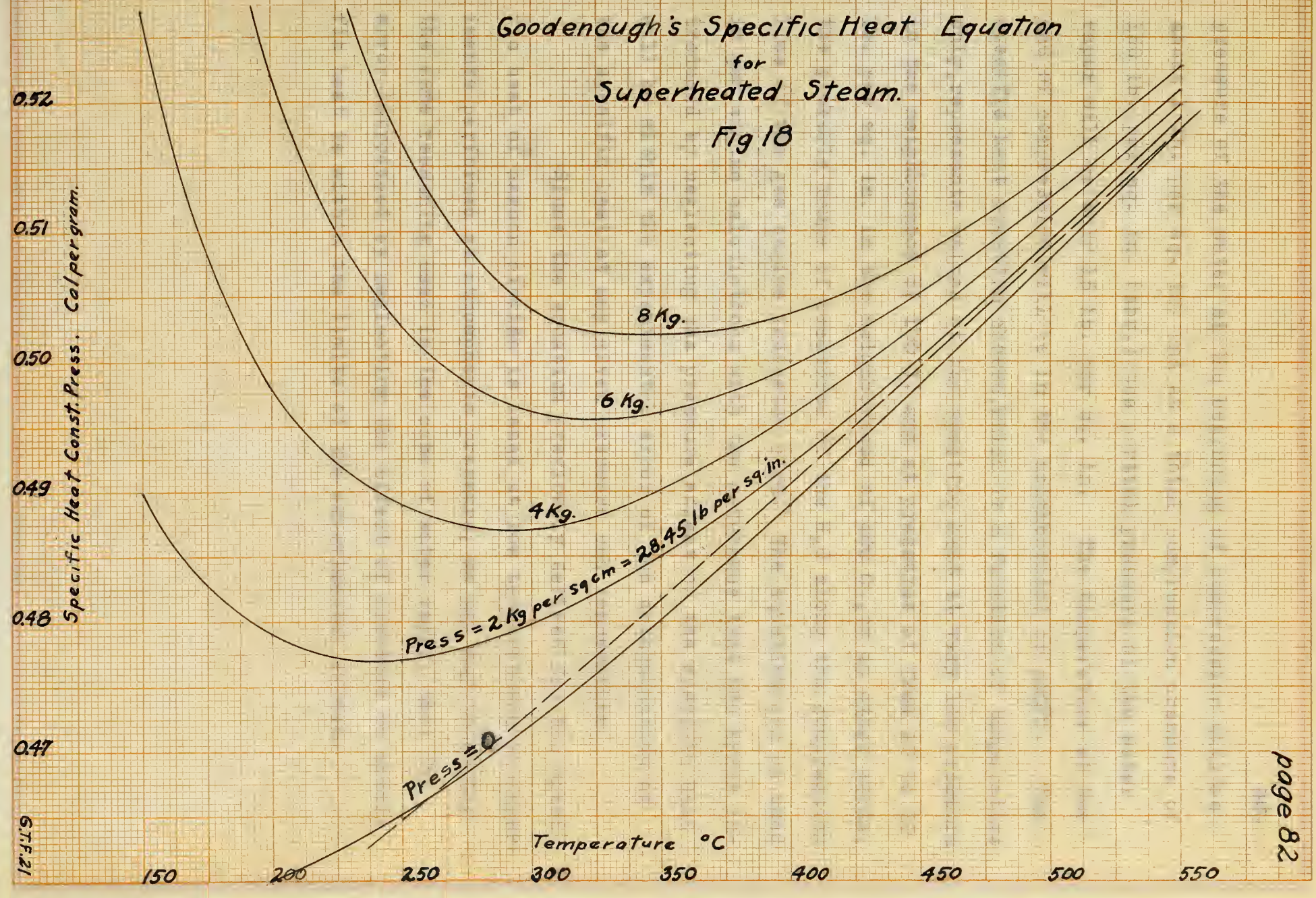
Temp °C.	150	200	250	300	350	400	450	500
C	0.450	0.457	0.465	0.473	0.482	0.491	0.500	0.509

Plotting the above values we have the curves shown in fig. 18, page 82. The dash line is the curve of the function of temperature only.

Above 550 C. it can be seen that the effect of pressure on the specific heat is so small as to be negligible. All temperatures in a gas engine except in the compression phase are greater than 550 C. so that the pressure does not effect these specific heat values. Assuming that the initial mixture of gases in the engine cylinder contained 10% of water vapor, which is probably above the maximum in any actual case, the partial

Goodenough's Specific Heat Equation for Superheated Steam.

Fig 18



G.T.F.21

Constant Specific Heat Expansion
Constant Pressure Steam
Fig 19
Temperature °C
Specific Heat Capacity
Pressure = 2 Kg/cm²
Pressure = 5 Kg/cm²
Pressure = 10 Kg/cm²
Pressure = 15 Kg/cm²
Pressure = 20 Kg/cm²
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
1050
1100
1150
1200
1250
1300
1350
1400
1450
1500

pressure of the water at the beginning of compression will be about 1 lb. per sq. in. and at a total compression pressure of 150 lb. per sq. in. (abs.) the partial pressure of the water vapor will be only 15 lb. per sq. in. The temperature at the end of compression will be in the neighborhood of 400°C. The specific heat equation chosen, which is a function of temperature only, represents values of the specific heat at very low pressure in the neighborhood of 100 C. and at pressures of from 10 to 20 lb. per sq. in. in the neighborhood of 400 C., or in other words, the probable range of pressures of the H_2O along the compression line of the gas engine indicator card. The equation can be used in gas engine calculations with the assurance that the error introduced by neglecting the pressure effect on the specific heat will be within the experimental error of the determination of the specific heat at any given pressure and temperature.

Since the equation previously derived for the specific heat of carbon dioxide is based at low temperatures on experiments performed at atmospheric pressure, we may say following the same reasoning used in the case of water vapor, that the error introduced by neglecting the effect of pressure on specific heat is within the limits of the experimental errors.

Specific heat of amorphous carbon: The experimental data available are as follows:

1. Regnault's value of 0.2415 for the mean specific heat of one gram of wood charcoal for the range 18 degrees to 98 degrees C.

2. De La Rive and Marcet's value of 0.1650 for the mean over the range 6 degrees to 15 degrees C. for wood charcoal.

3. Bettendorff and Wullner's value of 0.2040 for the range 24 degrees to 68 degrees C. for gas rhetort carbon.

4. Weber gives the following values for the mean specific heat of wood charcoal:

0^{o}-24^{o}C	0.1653	0^{o}- 224^{o}C	0.2385
0^{o}- 99^{o}C	0.1935		

5. Kunz gives the following values for the instantaneous specific heat of beechwood charcoal:

435^{o}C	0.243	1059^{o}C	0.362
561	0.290	1197	0.378
728	0.328	1297	0.381
925	0.358		

From the above data the following equation has been deduced for the instantaneous molecular specific heat of amorphous carbon. T is in degrees Centigrade absolute.

$$\gamma_p = 1.60 + 2.84 \cdot 10^{-3} T - 0.57 \cdot 10^{-6} T^2$$

A comparison between the experimental values and the values calculated from the above equation is given in the following table:

Temperature Centigrade absolute.	Molecular Specific Heat calc.	observed.	Investigator
291 - 371	2.477 (mean)	2.898	Regnault
279 - 288	2.359 "	1.980	De La Rive & Marcet
297 - 341	2.447 "	2.448	Bettendorff & Wullner
273 - 297	2.363 "	1.984	Weber
273 - 372	2.456 "	2.322	"
273 - 497	2.607 "	2.862	"
708	3.337 (inst.)	2.916	Kunz
834	3.573 "	3.468	"
1001	3.869 "	3.948	"
1198	4.187 "	4.272	"
1332	4.373 "	4.345	"
1470	4.543 "	4.512	"
1570	4.654 "	4.584	"

At the low temperatures the equation strikes about an average of the experimental data and at the higher temperatures agrees very well with the Kunz values as can be seen in fig. 19, page 86. The equation gives a maximum of 5.138 at T 2490 degrees C.(abs.) or 4022 degrees F.

Changing to the Fahrenheit scale, the equation becomes for the instantaneous molecular specific heat of amorphous carbon

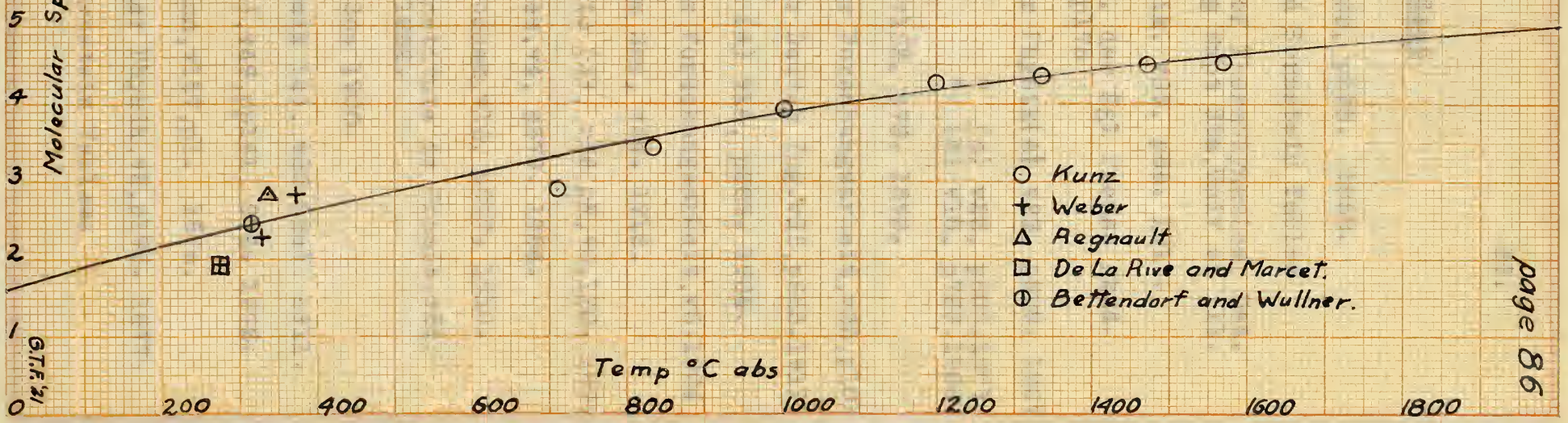
$$\gamma_p = 1.60 + 1.58 \cdot 10^{-3} T - 0.176 \cdot 10^{-6} T^2$$

Fig. 19

Specific Heat of Amorphous Carbon.

$\gamma = 1.60 + 2.84 \cdot 10^{-3} T - 0.57 \cdot 10^{-6} T^2$

Instantaneous T in deg. C abs.



G.T.F. 12

Fig. 19

Specific Heat of Amorphous Carbon

$S = 0.1720 + 0.384 \times 10^{-3} T$

S in cals. per gm. per degree C.
T in degrees Centigrade

Temp. °C cals.

Molecular Specific Heat

Water

Sugar | Coal | Coal | Coal | Coal | Coal | Coal | Coal | Coal | Coal | Coal

Temperature Coefficient of Specific Heat

Legend:
- Diamond
- Graphite
- Platinum
- Aluminum
- Magnesium
- Iron
- Nickel

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A P P E N D I X B

H E A T O F C O M B U S T I O N

Appendix B

Heat of Combustion

I. Hydrogen. Leaving out of consideration the work of investigators previous to 1848, we have the following brief outline of the methods used by the various investigators since that date for the determination of the heating value of hydrogen, and also the results obtained by each.

Andrews, in 1848, first used the bomb calorimeter. Hydrogen and oxygen collected over water were introduced into the bomb in the theoretical proportions for combustion. The gas mixture, under a total pressure of one atmosphere, was ignited by an electric spark, the heat generated being absorbed by water surrounding the bomb. Andrews found as the average of four experiments the higher heating value of one standard litre (0°C. 760mm.) of dry hydrogen at 20 degrees C. and constant volume to be 3036 calories. (20 degree calorie)

Favre and Silbermann in 1852 burned hydrogen with oxygen in a closed vessel at a constant pressure of 16 centimeters of water above atmospheric. This burning was accomplished by leading two metal tubes into a small metal chamber, one for hydrogen and one for oxygen. By regulating the flow of the gases a steady flame was maintained. The heat of combustion was absorbed by water which completely surrounded the combustion chamber. Since the flame was completely enclosed the water formed by the combustion could not escape and so was condensed.

At the beginning and end of each experiment the combustion chamber was weighed, the increase in weight being the water formed. Correction was made for the non-condensed water vapor within the combustion chamber by weighing the chamber filled with wet and then with dry gases. The difference is the weight of non-condensed vapor. This weight of vapor is multiplied by the latent heat of steam at 18 degrees C. and the result added to the experimental result. As the average of 6 experiments the higher heating value of 1 mol of hydrogen at 18 degrees C. and constant pressure was found to be 68,924 calories. (20 degree calories.)

J. Thomsen in 1873 using the same method as Favre and Silbermann with minor changes in the apparatus found the higher heating value of one mol of hydrogen at 18 degrees C. and at constant pressure to be 68,357 calories (20 degree cal.) This isthe average of three experiments.

In 1877 Schuller and Wartha used a Bunsen ice calorimeter wherein the heat of combustion is determined by measuring the amount of ice melted at 0 degrees C. The amount of ice melted is measured by the contraction in volume of a mixture of ice and water. Volume of ice melted times specific weight times latent heat of fusion of ice gives the heat absorbed by the ice. The closed end of a test tube projects into the mixture of ice and water. Inside of the test tube is placed a previously weighed glass combustion pipette. This combustion pipette consists simply of a small glass bulb into which are led two glass tubes, one for hydrogen and one for oxygen.

Burning occurs at constant pressure inside this bulb. Since there is no outlet the water formed condenses and remains in the bulb. At the end of an experiment the glass pipette is again weighed , the increase in weight being the water formed. The experiments lasted 3 to 4 hours so that the small amount of vapor left uncondensed in the pipette introduced a negligible error. As an average of 5 experiments the higher heating value of 1 mol of hydrogen at 0 degrees C. and at constant pressure was found to be 68,250 calories (mean cal. 0 degrees - 100 degrees C.)

In 1881 Than used the Bunsen ice calorimeter with a constant volume combustion pipette. In order to get an appreciable volume of gases in the pipette the calorimeter was quite large. Hydrogen and oxygen were introduced into the pipette under a total pressure of one atmosphere (Barometer 760 mm.) and exploded by an electric spark. The gases before combustion were saturated with water vapor so that all water vapor formed was condensed. The average result obtained from 5 experiments for the higher heating value of 1 mol of hydrogen burned at 0 degrees C. and at constant volume is 67,644 calories (15 degree cal.)

Berthelot in 1883 revived Andrew's bomb calorimeter and much improved it. The bomb was first filled with dry hydrogen under a pressure of 1 atmosphere. Wet oxygen was next introduced into the bomb from a cylinder of compressed oxygen until the total gas pressure in the bomb was about 1.7 atmospheres. The excess of oxygen was used because the compressed oxygen con-

tained a small percentage of nitrogen. The mixture was exploded by an electric spark. Since all the water vapor formed is condensed no correction is needed. Berthelot gives as the higher heating value of 1 mol of hydrogen at constant volume and at 10 degrees C. 68,000 calories. (10 degree cal.)

In 1903 Mixter, at Yale University, made further improvements on the bomb calorimeter. Dry hydrogen was first introduced into the bomb at atmospheric pressure (bar. 14.743 lb. per sq. in.). The weight of hydrogen present was calculated from its known pressure, temperature, and volume. Dry oxygen was next introduced into the bomb until the total pressure was in excess of 1½ atmospheres. The average of 14 experiments by Mixter gives for the higher heating value of 1 mol of hydrogen at 18 degrees C. and at constant volume, omitting the correction for non-condensed water vapor which will be considered later, 66,835 calories (20 degrees cal.)

The latest work done on the heating value of hydrogen is that of G. Rumelin in 1907. He used a bomb calorimeter of more elaborate designthan those previously used. Dry hydrogen and oxygen in the theoretical proportions for combustion were introduced into the bomb under a total pressure of 1 atmosphere (Bar. 14.32 lb. per sq. in.) As an average of six experiments omitting the correction for non-condensed vapor left in the bomb, the observed result for the higher heating value of 1 mol of hydrogen at 18 degrees C. and at constant volume was 66,940 calories. (20 degree cal.)

In order to put the above values on a comparative basis we shall change them all from the French system to the English system of units and use the mean B.T.U. in the range 32 - 212 degrees F. Also the lower heating value will be calculated in each case.

To convert to the mean B.T.U. we have from Callendar's equation for the specific heat of water taking the mean B.T.U. (32 to 212 degrees F.) as unity the following correction factors:

Temperature Degrees C.	Degrees F.	Correction factor	Log correction factor
10	50	1.00150	0.0006499
15	59	0.99962	$\bar{1}.9998352$
20	68	0.99842	$\bar{1}.9993100$

We shall use the following notation:

H_v = lower heating value per mol at constant volume,

H_p = " " " " " " " pressure,

H'_v = higher " " " " " " volume,

H'_p = " " " " " " " pressure.

The experimental methods outlined above fall into the two general classes, i.e., burning at constant volume and at constant pressure.

To deduce the lower heating value from experimental results given we shall use the following method: As the hot gases are cooling after combustion no condensation of the water vapor occurs until the temperature of the gases falls below the saturation temperature corresponding to the partial pressure of the water vapor constituent. Condensation then occurs between the saturation temperature and the final temperature of the

gases. If the initial gases were saturated with water vapor, all the water formed by the combustion will condense if the products of combustion are brot back to the initial temperature since the amount of water vapor required to saturate a given volume of any gas is dependent on the temperature only. If the initial gases are dry, however, that portion of the water vapor formed which is required to saturate the given volume of gas at the final temperature will remain as vapor. To get the higher heating value when the initial gases are dry the latent heat of the non-condensed vapor must be added to the observed results. By definition the lower heating value of a gas is the amount of heatgiven out during the combustion of the gas considering the water formed to remain in the vapor state when the products of combustion are cooled down to the initial temperature. The difference, then, between the higher heating value and the lower heating value is the difference between the amount of heat given out by the hot gases in cooling in the first place with condensation and in the second place cooling without condensation.

The heat given up with condensation at constant volume in cooling from the saturation temperature to the final temperature is

$$_1Q'_2 = u_1'' - (u'_2 + x\rho)$$

where

u''_1 = thermal energy of 1 lb. of steam at the saturation point in the cooling of the products of combustion.

u_2' = thermal energy of 1 lb. of liquid water at the final temperature.

x = fraction of water formed remaining non-condensed.

ρ = internal latent heat of 1 lb. of steam at final temperature.

The heat given up by the water vapor in cooling at constant volume from the saturation temperature to the final temperature considered as a non-condensable gas is

$$,Q_2 = \int_{T_2}^{T_1} \gamma_v \, dt.$$

where γ_v = instantaneous specific heat of 1 mol of water vapor. Representing specific heat by the following function

$$\gamma_v = a + bT + fT^2$$

we have upon substitution and integration

$$,Q_2 = a(T_1 - T_2) + \tfrac{1}{2}b(T_1^2 - T_2^2) + \tfrac{1}{3}f(T_1^3 - T_2^3)$$

$$H_v' - H_v = ,Q_2' - ,Q_2$$

$$H_v' - H_v = \left[u_1'' - (u_2' + x\rho)\right] - \left[a(T_1 - T_2) + \tfrac{1}{2}b(T_1^2 - T_2^2) + \tfrac{1}{3}f(T_1^3 - T_2^3)\right]$$

The temperature at which saturation first occurs in the cooling process at constant volume is determined by the following. Knowing the pressure, temperature, and composition of the initial gases the total volume can be determined. This is also the volume of the resulting water vapor from which the volume per lb. is easily determined. The saturation temperature corresponding to this specific volume can be formed in the steam tables and is the temperature desired.

The heat given up with condensation at constant pressure by the gases in cooling from the temperature at which

saturation is first reached to the final temperature is

$$_1Q'_2 = i''_1 - (i'_2 + xr)$$

where

i''_1 = thermal head of 1 lb. of steam at temperature in cooling at which saturation is first reached

i'_2 = thermal head of 1 lb. of liquid water at final temperature.

r = latent heat of vaporization of 1 lb. of steam at final temperature.

x = fraction of water formed remaining non-condensed.

The heat given up by the water vapor in cooling at constant pressure from the saturation temperature to the final temperature is

$$_1Q_2 = \int_{T_2}^{T_1} \gamma_p \, dt$$

γ_p = instantaneous specific heat at constant pressure.

$$\gamma_p = a' + bT + fT^2$$

$$_1Q_2 = a'(T_1 - T_2) + \tfrac{1}{2}b(T_1^2 - T_2^2) + \tfrac{1}{3}f(T_1^3 - T_2^3)$$

$$H'_p - H_p = {}_1Q'_2 - {}_1Q_2$$

$$H'_p - H_p = \left[i''_1 - (i'_2 + xr)\right] - \left[a'(T_1 - T_2) + \tfrac{1}{2}b(T_1^2 - T_2^2) + \tfrac{1}{3}f(T_1^3 - T_2^3)\right]$$

Knowing the pressure at which combustion occurs and the composition of the products, the partial pressure of the water vapor in the products can be determined. The saturation temperature corresponding to this pressure can be found from the steam tables and is the saturation temperature desired.

The calculations of the lower heating values for the constant volume cases are as follows:

Andrews. Since the initial gases are under atmospheric pressure and saturated with water vapor the reaction is

$$H_2 + \tfrac{1}{2}O_2 + y\ H_2O \rightarrow (1-y)\ H_2O$$

From Goodenough's steam tables the saturation pressure at 68 degrees F. is 0.339 lb. per sq. in.

$$\frac{y}{1.5\ y} = \frac{0.339}{14.7}$$

Solution gives y 0.0354 mols.

Volume of 1.5354 mols at 68 degrees F.

$$= 1.5354 \times 380.6 \times \frac{528}{522} = 596.1 \text{ cu. ft.}$$

380.6 cu. ft. = volume of 1 mol at 62 degrees F. and 14.7 lb. per sq. inch.abs.

Volume of 1 lb. of H_2O in final mixture

$$= \frac{596.1}{18 \times 1.0354} = 31.715 \text{ cu. ft.}$$

The saturation temperature corresponding to this volume is 203°F.

$u_1'' = 1076.2 \qquad u_2' = 36.1 \qquad x = 0$

$${}_1Q_2' = 18(1076.2-36.1) = 18{,}722 \text{ B.T.U.}$$

$${}_1Q_2 = \int_{T_2}^{T_1} \gamma_v\, dt = 5.04(663-528) + \frac{1.25 \cdot 10^{-3}}{2}(663^2-528^2) + \frac{0.20}{3}\,10^{-6} \times (663^3-528^3)$$

$${}_1Q_2 = 791$$

$$H_v' - H_v = 18722 - 791 = 17{,}931$$

$$H_v' = 22.412 \times 3036 \times 1.8 \times 0.99842 = 122{,}000 \text{ B.T.U. per mol.}$$

$$H_v = 122{,}000 - 17931 = 104{,}069$$

$$H_p = H_v - RT\Sigma\gamma = H_v + T$$

$$H_p = 104{,}069 + 528 = 104{,}597 \text{ B.T.U. per mol at 68 degrees F.}$$

Than: Method same as for Andrew's case.

Initial temperature =32 degrees F.

Saturation pressure at 32 degrees F. = 0.0887

y = 0.009

Volume of 1 lb. water vapor in products = $\frac{358.7 \times 1.509}{18 \times 1.009}$ = 2980 cu.ft.

Saturation temperature =206.3 degrees F.

u_1'' =1077.2 u_2' = 0 x = 0

Q_2' = 18×1077.2 =19,389

Q_2 =1016

H_v' =67644 ×1.8 × 0.99962 =121,713

$H_v' - H_v$ = 19389 - 1016 =18,373

H_v = 121,713 - 18,373 = 103,340 B.T.U. per mol.

H_p =103340 +492 = 103,832 B.T.U. per mol at 32 degrees F.

To change this value to H at 62 degrees F. we have

$$H_{P_{62}} = H_{P_{32}} + \int_{492}^{522} \left[\gamma_{P_{H_2}} + \tfrac{1}{2}\gamma_{P_{O_2}} - \gamma_{P_{H_2O}}\right] dt$$

$$\gamma_{P_{H_2}} = 6.5 + 0.5 \cdot 10^{-3} T$$

$$\tfrac{1}{2}\gamma_{P_{O_2}} = \frac{3.25 + 0.2778 \cdot 10^{-3} T}{\text{sum} = 9.75 + 0.7778 \cdot 10^{-3} T}$$

$$\gamma_{P_{H_2O}} = \frac{7.03 + 1.25 \cdot 10^{-3} T + 0.2 \cdot 10^{-6} T^2}{\text{Dif} = 2.72 - 0.4722 \cdot 10^{-3} T - 0.2 \cdot 10^{-6} T^2}$$

$$H_{P_{62}} = H_{P_{32}} + \left[2.72(522-492) - 0.2361 \cdot 10^{-3}(522^2 - 492^2) - \frac{0.2}{3} \cdot 10^{-6}(522^3 - 492^3)\right] = H_{P_{32}} + 74$$

$H_{P_{62}}$ = 103,906 B.T.U. per mol.

Berthelot:

Initial partial pressure of dry hydrogen =14.7 lb.per.sq.in.

Total pressure of initial gases about 1.7 atmospheres.

Initial and final temperatures = 50 degrees F.

Initial gases saturated with H_2O

Since the partial pressure of the dry hydrogen in the initial gases is 1 atmosphere, the partial pressure of the water vapor formed in the products will be 1 atmosphere, at 50 degrees F. when considered non-condensed.

Partial pressure of water vapor used to saturate initial gases at 50 degrees F. = 0.18 lb. per sq. in.

Therefore: Total partial pressure of H_2O in products at 50 degrees F. = 14.70 + 0.18 = 14.88 lb. per sq. in.

Volume of 1 lb. of water vapor in products of combustion

$$= \frac{380.6}{18} \times \frac{510}{522} \times \frac{14.70}{14.88} = 20.408 \text{ cu. ft. per lb.}$$

Saturation temperature = 227 degrees F.

$u_1'' = 1083.0$ $\quad u_2' = 18.1$ $\quad x = 0$

$Q_2' = 18(1083.0-18.1) = 19{,}168$ B.T.U. per mol.

$Q_2 = 1037$ B.T.U. per mol.

$H_v' - H_v = 19168 - 1037 = 18{,}131$

$H_v' = 68{,}000 \times 1.8 \times 1.00150 = 122{,}583$ B.T.U. per mol.

$H_v = 122{,}583 - 18131 = 104{,}452$

$H_p = 104452 + 510 = 104{,}962$ B.T.U. per mol at 50 degrees F.

Mixter:

Initial gases dry at 64 degrees F.

Initial pressure of hydrogen = 14.743 lb. per sq. in.

Final pressure of water vapor formed considered non-condensed is therefore 14.743 lb. per sq. in.

Volume of 1 lb. of water vapor in products of combustion

$$= \frac{380.6}{18} \times \frac{524}{522} \times \frac{14.700}{14.743} = 21.164 \text{ cu. ft.}$$

Saturation temperature = 225 degrees F. (from steam tables)

$u_1'' = 1082.5$ $\quad u_2' = 32.1$ $\quad \rho = 998.4$

Saturation pressure at 64 degrees F = 0.295 lb. per sq. in.

Therefore: $x = \frac{0.295}{14.743} = 0.0200$

$$Q_2' = 18\left[1082.5 - (32.1 + 0.02 \times 998.4)\right] = 18547$$

$Q_2 = 945$

$H_v' - H_v = 18547 - 945 = 17{,}602$ B.T.U.

H_v' (observed) = 66,835 x 1.8 x 0.99842 = 120,112 B.T.U. per mol.

$H_v = 120{,}112 - 17{,}602 = 102{,}510$

$H_p = 102{,}510 + 524 = 103034$ B.T.U. per mol. at 62 degrees F.

Rumelin:

Dry hydrogen and oxygen

Total pressure = 1 atmosphere = 14.32 lb. per sq. in.

Initial temperature = 64 degrees F.

Partial pressure of water vapor as products non-condensed

= 2/3 x 14.32 = 9.55 lb. per sq. in.

Volume of 1 lb. water vapor = $\frac{380.6}{18} \times \frac{524}{522} \times \frac{14.7}{9.55} = 32.673$

Saturation temperature = 202 degrees F.

Saturation pressure at 64 degrees F. = 0.295 lb. per sq. in.

$x = 0.295/9.55 = 0.0323$

$u_1'' = 1075.9$ $\quad u_2' = 32.1$ $\quad \rho = 998.4$

$$Q_2' = 18\left[1075.9 - (32.1 + 0.0323 \times 998.4)\right] = 18{,}209 \text{ B.T.U. per mol.}$$

$Q_2 = 807$

$H_v' - H_v = 18209 - 807 = 17,400$

H_v' (Observed) $= 66,940 \times 1.8 \times 0.99842 = 120,300$

$H_v = 120,300 - 17,400 = 102,900$

$H_p = 102,900 + 524 = 103,424$ B.T.U. per mol at 64 degrees F.

The calculations for the lower heating values in the constant pressure cases are as follows:

Favre and Silbermann,

Temperature of combustion = 64 degrees F.

Pressure of combustion = 16 cm. of water above atmospheric = 14.70 + 0.23 = 14.93 lb. per sq. in.

Since H_2O is the only product of combustion, we have

Saturation temperature at 14.93 lb. per sq. in. = 213°F.

$i_2'' = 1152.1$ $\quad i_2' = 32.1$ $\quad x = 0$

$Q_2' = 18(1152.1 - 32.1) = 20,160$ B.T.U. per mol

$\gamma_{p_{H_2O}} = 7.03 + 1.25 \cdot 10^{-3} T + 0.20 \cdot 10^{-6} T^2$

$Q_2 = 7.03 (673 - 524) + \frac{1}{2} 1.25 \cdot 10^{-3} (673^2 - 524^2)$

$+ \frac{0.20}{3} 10^{-6} (673^3 - 524^3) = 1169$

$H_p' - H_p = 20,160 - 1169 = 18,991$

H_p' (observed) $= 68,924 \times 1.8 \times 0.99842 = 123,866$ B.T.U./mol 64°F.

$H_p = 123,866 - 18,991 = 104,875$ B.T.U. per mol at 64°F.

Thomsen:

Temperature of combustion = 64 degrees F.

Pressure of combustion = 14.70 lb. per sq. in.

Since H_2O alone is the product of combustion, the pressure of H_2O in the products = 14.70 lb. per sq. in.

Saturation temperature = 212 degrees F.

$i_1'' = 1151.7$ $\quad i_2' = 32.1$ $\quad x = 0$

$_1Q_2' = 18(1151.7 - 32.1) = 20,153$

$_1Q_2 = 7.03\,(672-524) + \frac{1}{2}1.25\cdot10^{-3}\,(672^2-524^2) + \frac{0.2}{3}(672^3-524^3)\cdot10^{-6}$

$= 1162$

$H_p' - H_p = 20,153 - 1162 = 18,991$

H_p (observed) $= 68,357 \times 1.8 \times 0.99842 = 122,849$

$H_p = 122,849 - 18,991 = 103,858$ B.T.U./mol at 64 degrees F.

Schuller and Wartha:

Temperature of combustion = 32 degrees F.

Pressure of combustion = 14.7 lb. per sq. in.

H_2O only as product of combustion

Saturation pressure = 212 degrees F.

$i_1'' = 1151.7$ $\quad i_2' = 0$ $\quad x = 0$

$_1Q_2' = 18 \times 1151.7 = 20,731$

$_1Q_2 = 1408$

$H_p' - H_p = 20731 - 1408 = 19,323$ B.T.U.

H_p (observed) $= 68250 \times 1.8 = 122852$

$H_p = 122852 - 19323 = 103529$ B.T.U. per mol at 32 degrees F.

As before (Than page 97.)

H_p (at 62 degrees F.) $= 103529 + 74 = 103,603$ B.T.U. per mol.

Collecting results and neglecting the small correction necessary to transfer the various values to the heat of combustion at 62 degrees F. we have the following table of values for the lower heating value of hydrogen at constant pressure and at 62 degrees F.

Date	Investigator	Value
1848	Andrews	104,597
1852	Favre and Silbermann	104,875
1873	Thomsen	103,858
1877	Schuller and Wartha	103,603
1881	Than	103,906
1883	Berthelot	104,962
1903	Mixter	103,034
1907	Rumelin	103,424

We shall omit the values of Andrews, Favre and Silbermann, and Berthelot as being obviously high. We shall weigh the remaining five values according to the following table; and take the average as our final result for the lower heating value of hydrogen burned at 62 degrees F. and at constant pressure. Thomsen value is given double weight because of the general accuracy of his experiments and because his result is the average of seven experiments in which a total of 18 grams of water were formed, this being a much larger amount than that formed in the experiments of any of the other investigators. The Mixter and Rumelin values are given the weight of three because of the comparatively recent dates at which their work was done. Also Mixter's value is the average of fourteen experiments all of which are within 1.3% of the average and Rumelin's value is the average of 7 experiments all of which are within 0.7% of the average.

Investigator.	Wt. of value in taking average.	Value.
Thomsen	2	103,858
Schuller and Wartha	1	103,603
Than	1	103,906
Mixter	3	103,034
Rumelin	3	103,424
	Average	103,459

As our final result we shall take the rounded value for hydrogen as H_p = 103,450 B.T.U. per mol at 62 degrees F.

II. Carbon Monoxide.

We have the following experimental results available for the heating value of carbon monoxide.

Date	Investigator.	Value	Temperature
1848	Andrews	3057 cal/litre at cons.vol.	15°C.
1852	Favre and Silbermann	2402.7 cal/gram " " press.	18°C.
1873	Thomsen	67960 cal/mol " " "	18°C.
1881	Berthelot	68200 " " " " "	10°C.

Andrews and Berthelot used the bomb calorimeter. Favre and Silbermann and Thomsen used the same apparatus as they did for hydrogen except that the products of combustion were led out of the combustion chamber through a coil of small pipe of considerable length which was immersed in the water of the calorimeter, thus insuring that the products of combustion were brought back to the initial temperature.

Transferring these results into mean B.T.U. per mol at constant pressure using Callendar's specific heat ratios and neglecting the correction to 62 degrees F., we have the following for H_p at 62 degrees F.

Andrews 123,800
Favre and Silbermann..... 120,900
Thomsen..... 122,130
Berthelot..... 122,920

Andrews' value cannot be considered because of the imperfection of his method. He took only one reading of the

water temperature in his calorimeter after combustion and that one just thirty seconds after combustion occurred. Due to the design of his apparatus, the thermometer had to be removed in order to rotate the apparatus which means was used to keep the water at a uniform temperature. To get the temperature of the water the rotation was stopped and the thermometer inserted. It can be seen that this manipulation is subject to many errors.

The Carbon monoxide used by Favre and Silbermann in their experiments contained about 3% hydrogen by weight. The correction for the heat of combustion of this hydrogen content amounted to about 30% of the heat resulting from the combustion as observed in any one determination. The possibility of error in this correction is very great because of the methods of gas analysis in use at that time and also because it automatically brings in all the errors of their determination of the heat of combustion of hydrogen.

Of the two remaining values we choose that of Thomsen's in favor of Berthelots for the following two reasons. First, for any given determination the volume of gas used by Thomsen was about six times that used by Berthelot, this tending to reduce Thomsen's error. Second, Berthelot's result is the average of five experiments where a total of about 1.3 liters of carbon monoxide were burned, while Thomsen's result is the average of 10 closely accordant experiments where in a total of

about 16 litres of carbon monoxide were burned. The first six of the experiments were performed in one calorimeter while the last four were performed in another larger calorimeter. The average result of the first group of experiments is exactly equal to the average of the last two.

We have, therefore, as the heating value of 1 mol of carbon monoxide at constant pressure at 62 degrees F. in terms of the mean B.T.U. the following:

$$H_p = 122,130$$

III. Methane, CH_4

We have the following data available on the heating value of methane:

Date	Investigator	Temp degrees C.	Higher heating value cal. per mol.
1848	Andrews	15	209,728 constant vol.
1852	Favre and Silbermann	18	209,000 " press
1880	Thomsen	20	213,530 " "
1881	Berthelot	18	212,400 " vol.

The methane used by Andrews was obtained from a a stagnant pool and contained a large percentage of nitrogen which invalidates his result. It is also very probable that the Favre and Silbermann value is low because of impurities in their gas.

Thomsen generated his methane from zinc methyl and hydrochloric acid, and purified it by bubbling thru cuprous chloride solution. The above result is from Thomsen's latest work on

methane, and is the average of nine experiments which show a maximum variation of 1.1%. The calorimeter used was of the constant pressure type, the products of combustion being led out thru a long tube winding around the combustion chamber as described before. Correction was made for the non-condensed vapor in the products of combustion, this correction being very small.

The Berthelot result is the average of four determinations made with his bomb calorimeter. These four experiments show a variation of 1.6%.

In order to compare Thomsen's and Berthelot's values we shall reduce them both to the lower heating value in mean B.T.U. per mol at 62 degrees F.

Thomsen: Methane was burned with the theoretical required oxygen at constant pressure of 1 atmosphere and temperature at 62 degrees F. Reaction is $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Partial pressure of H_2O vapor in products is

$$P_{H_2O} = 2/3 \times 14.7 = 9.8 \text{ lb. per sq. in.}$$

Saturation temperature at this pressure is 192 degrees F.

$i_1'' = 1143.9 \qquad i_2' = 30.1 \qquad x = 0$

$Q_2' = 36(1143.90 - 30.1) = 40,097$

$Q_2 = 2037$

$H_p' - H_p = 40,097 - 2037 = 38,060$ B.T.U. per mol CH_4

$H_p' = 213,530 \times 1.8 \times 0.99842 = 383,750$ mean B.T.U. per mol.

$H_p = H_v = 383,750 - 38,060 = 345,690$ B.T.U. per mol.

Berthelot: Methane was burned with excess oxygen at constant volume and temperature of 62 degrees F.

Pressure of dry CH_4 in initial mixture = 1 atm. = 14.7 lb. per sq. in. Total initial pressure = 3.4 atm. (approx)

Reaction is

$$CH_4 + 2.4O_2 \rightarrow CO_2 + 2H_2O + 0.4O_2$$

Partial pressure of water vapor formed in products

$= 2 \times 14.7 = 29.4$ lb. per sq. in.

Partial pressure of water vapor required to saturate initial gases at 62 degrees F. = 0.275 lb. per sq. in.

$P_{H_2O} = 29.4 + 0.275 = 29.675$ lb. per sq. in.

Volume of H_2O per pound in products at 62 degrees F.

$$= \frac{14.7}{29.672} \times \frac{380.6}{18} = 10.475 \text{ cu. ft. per lb.}$$

Saturation temperature = 267 degrees F.

$u_1'' = 1093.4$ $\quad u_2' = 30.1$ $\quad x = 0$

$Q_2' = 36(1093.4 - 30.1) = 38279$

$Q_2 = 2415$

$H_v' - H_v = 38279 - 2415 = 35864$

$H_v' = 212400 \times 1.8 \times 0.99842 = 381710$

$H_v = H_p = 381710 - 35864 = 345846$ B.T.U. per mol.

Thomsen	H	345690
Berthelot	H	345846
average		345768

Lower heating value of methane at 62 degrees F.

= 345770 mean B.T.U. per mol.

IV. Acetylene (C_2H_2)

We have the following experimental data on the heating value of acetylene:

Date	Investigator	Temp. degrees C.	Higher heating value cal. per mol
1880	Thomsen	19	310050 const. press.
1881	Berthelot	18	314900 " vol.
1906	Mixter	20	311400 " " (observed heat not corrected)

The methods used by the above investigators are the same as described previously for other gases.

For the lower heating values we have the following calculations:

Thomsen: Acetylene burned with the theoretical required oxygen at constant pressure of one atmosphere and temperature of 66 degrees F. = 526 degrees F. (abs.)

The reaction is $C_2H_2 + 2\frac{1}{2}O_2 \rightarrow 2CO_2 + H_2O$

The partial pressure of H_2O vapor in products is

$P_{H_2O} = 1/3 \times 14.7 = 4.9$ lb. per sq. in.

The saturation temperature at this pressure is 161 degrees F.

$i_1'' = 1131.2 \qquad i_2' = 34.08 \qquad x = 0$

$Q_2' = 18(1131.2 - 34.1) = 19748$ B.T.U. per mol of C_2H_2

$Q_2 = 742$

$H_p' - H_p = 19748 - 742 = 19006$ B.T.U. per mol.

$H_p' = 310050 \times 1.8 \times 0.99842 = 557200$ B.T.U. per mol

$H_p = 557200 - 19000 = 538200$ B.T.U. per mol.

Berthelot: Acetylene burned at constant volume with excess oxygen at temperature of 62 degrees F.

Pressure of dry C_2H_2 in initial mixture = one atmosphere

= 14.7 lb. per sq. in.

Reaction is $C_2H_2 + 3O_2 \rightarrow 2CO_2 + H_2O + \frac{1}{2}O_2$

Partial pressure of water vapor required to saturate initial gases at 62 degrees F. = 0.275 lb. per sq. in.

$P_{H_2O} = 14.7 + 0.275 = 14.975$

Volume of H_2O per pound in products at 62 degrees F.

$$= \frac{14.7}{14.975} \times \frac{380.6}{18} = 20.756 \text{ cu. ft.}$$

Saturation temperature for this volume is 194 degrees F. = 654 °F abs.

$u_1'' = 1073.5$ $u_1' = 30.1$ $x = 0$

$Q_2' = 18(1073.5-30.1) = 18781$

$Q_2 = 771$

$H_v' - H_v = 18781 - 771 = 18010$

$H_v' = 314900 \times 0.99842 \times 1.8 = 565920$ B.T.U. per mol.

$H_v = 565920 - 18010 = 547910$

$H_p = 547910 + 522 = 548432$ B.T.U. per mol.

Mixter: Initial pressure of acetylene = 14.65 lb. per sq. in. Initial gases dry at 20 degrees C. = 68 degrees F.

Therefore, final pressure of water vapor considered non-condensed

= 14.65 lb. per sq. in.

Volume of 1 lb. of water vapor in products of combustion

$$= \frac{380.6}{18} \times \frac{528}{522} \times \frac{14.70}{14.65} = 21.46 \text{ cu. ft.}$$

Saturation temperature = 224 degrees F (from steam tables)

$u_1'' = 1082.2$ $u_2' = 36.1$ $\rho = 890.2$

Saturation pressure at T = 68 degrees F. = 0.339 lb. per sq.in.

$x = 0.339/14.65 = 0.0231$

$Q_2' = 18[u_1'' - (u_2' + x\rho)] = 18459$

$Q_2 = 915$

$H_v' - H_v = 18459 - 915 = 17544$

H_v (observed) = 311400×1.8×0.99842 = 559630

$H_v = 559630 - 17544 = 542086$

$H_p = 542086 + 528 = 542614$ B.T.U/mol C_2H_2

Collecting results we have for the lower heating value of acetylene at constant pressure and 62 degrees F.:

Thomsen	538,200
Berthelot	548,432
Mixter	542,614

Weighing Thomsen's value 2, Berthelot's 1, and Mixter's 3, we have as the average

H_p = 542,110 B.T.U. per mol. at constant pressure and 62° F.

V. Ethylene (C_2H_4)

Experimental data on the heating value of ethylene:

Date	Investigator	Temp. degrees C.	Higher heating value Cal.per mol.
1880	Thomsen	17.9	333350 const. press.
1881	Berthelot-Matignon	16.8	340000 " vol.
1901	Mixter	18.8 (Obs.)	345080 " "

For the lower heating values we have the following calculations:

Thomsen: Ethylene burned with the theoretical amountof oxygen at a pressure of one atmosphere =14.7 lb. per sq. in, and temperature of 64 degrees F. Reaction is $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

Partial pressure of H_2O vapor in products considered non-condensed is $P_{H_2O} = \frac{1}{2} \times 14.7 = 7.35$ lb. per sq. in.

Saturation temp. at 7.35 lb. per sq. in. = 179 degrees F.

$i_1'' = 1138.7$ $\quad i_2' = 32.1$ $\quad x = 0$

$Q_2' = 36(1138.7-32.1) = 39838$

$Q_2 = 1800$

$H_p' - H_p = 39838 - 1800 = 38038$ B.T.U. per mol C_2H_4

$H_p' = 333350 \times 1.8 \times 0.99842 = 599070$

$H_p = 599070 - 38038 = 561030$ B.T.U. per mol C_2H_4

Berthelot: Ethylene burned at constant volume with excess of oxygen $\quad$ T = 62 degrees F.

Pressure of dry C_2H_4 in initial mixture =1 atm. =14.7 lb.per sq. in.

$C_2H_4 + 3\frac{1}{2}O_2 \rightarrow 2CO_2 + 2H_2O + \frac{1}{2}O_2$

Partial pressure of H_2O vapor in products of combustion considered non-condensed = $2 \times 14.7 = 29.4$ lb. per sq. in.

Partial pressure of water vapor required to saturate initial gases at 62 degrees F. = 0.275 lb. per sq. in.

$P_{H_2O} = 29.4 + 0.275 = 29.675$ lb. per sq. in.

Volume of H_2O per pound in products at 62 degrees F.

$$= \frac{14.7}{29.672} \times \frac{380.6}{18} = 10.475 \text{ cu. ft. per lb.}$$

Saturation temperature = 267 degrees F.

$u_1'' = 1093.4$ $\quad u_2' = 30.1$ $\quad x = 0$

$Q_2' = 36(1093.4-30.1) = 38279$ B.T.U. per mol C_2H_4

$_1Q_2 = 2415$

$H_v' - H_v = 38279 - 2415 = 35864$

$H_v' = 340000 \times 1.8 \times 0.99962 = 611760$

$H_v = 611760 - 35864 = 575896$

$H_v = H_p = 575896$

Mixter: Initial pressure of ethylene = 14.7 lb. per sq. in. at 18.8 degrees C. = 66 degrees F. Initial gases dry.

Final pressure of water vapor considered non-condensed = $2 \times 14.7 = 29.4$ lb. per sq. in.

Volume of 1 lb. of water vapor in products of combustion considered non-condensed = $\frac{380.6}{18} \times \frac{526}{522} \times \frac{14.7}{29.4} = 10.653$ cu. ft.

Saturation temperature = 266 degrees F. (from steam tables)

$u_1' = 1093.1 \qquad u_2' = 34.1 \qquad \rho = 858.8$

Saturation pressure at T = 66 degrees F = 0.316 lb. per sq.in.

$x = 0.316/29.4 = 0.0011$

$_1Q_2' = 36\,[1093.1 - (34.1 + 0.0011 \times 858.8)] = 38092$ B.T.U.per mol C_2H_4

$_1Q_2 = 2360$

$H_v' - H_v = 38092 - 2360 = 35732$

$H_v' = 345080 \times 1.8 \times 0.99842 = 620160$

$H_v = H_p = 620160 - 35732 = 584430$

Collecting results we have for the lower heating value of ethylene (C_2H_4) per mol:

Thomsen	561,030 B.T.U. per mol
Berthelot	575,900
Mixter	584,430

Weighing Thomsen's value 2, Berthelot's 1, and Mixter's 3, we have the following value for the lower heating value of

ethylene at 62 degrees F.at constant pressure:

H_p = 575,210 B.T.U. per mol.

VI. Ethane (C_2H_6)

Experimental values:

Date	Investigator	Temp.degrees C.	Heating value(higher) Cal. per mol.
1893	Berthelot	13	370,900 const. volume
1905	Thomsen	18	370,440 " pressure

Reduction to lower heating value:

Berthelot: Ethane burned at constant volume with excess oxygen at temperature of 55 degrees F.

Pressure of dry C_2H_6 in original mixture = 1 atm. = 14.7 lb. per sq. inch.

Reaction is $C_2H_6 + 4O_2 \rightarrow 2CO_2 + 3H_2O + \frac{1}{2}O_2$

Partial pressure of water vapor formed in products considered non-condensed is $3 \times 14.7 = 44.1$ lb. per sq. in.

Partial pressure of water vapor required to saturate initial gases at 55 degrees F. = 0.214 lb. per sq. in.

$P_{H_2O} = 44.1 + 0.214 = 44.314$ lb. per sq. in.

Volume of H_2O per pound in products at 55 degrees F.

$$= \frac{380.6}{18} \times \frac{515}{522} \times \frac{14.7}{44.314} = 6.920 \text{ cu. ft.}$$

Saturation temperature = 295 degrees F. (steam tables)

$u_1'' = 1099.8$ $\quad u_2' = 23.1$ $\quad x = 0$

$Q_2' = 54(1099.8 - 23.1) = 58,142$

$Q_2 = 4260$

$H_v' - H_v = 58142 - 4260 = 53,882$

$H_v' = 370,900 \times 1.8 \times 0.99962 = 667,360$

$H_v' = 667,360 - 53,882 = 613,478$

$H_p = H_v + T = 613,478 + 515 = 613,993$

Thomsen: Ethane burned at constant pressure of 1 atm.=14.7 lb. per sq. in, with the theoretical amount of oxygen at 18 degrees C. = 64 degrees F. Reaction is

$$C_2H_6 + 3\tfrac{1}{2}O_2 \rightarrow 2CO_2 + 3H_2O$$

Partial pressure of water vapor in products considered non-condensed is

$P_{H_2O} = 3/5 \times 14.7 = 8.81$ lb. per sq. in.

Saturation temperature at 8.81 lb. per sq. in. = 187 degrees F

$i_1'' = 1141.9 \qquad i_2' = 32.1 \qquad x = 0$

$_1Q_2' = 54(1141.9-32.1) = 59,929$ B.T.U. per mol C_2H_6

$$_1Q_2 = 3\left[7.03(647-524) + \tfrac{1}{2}\,1.25\cdot10^{-3}(647^2-524^2) + 1/3\cdot0.2(647^3-524^3)\cdot10^{-6}\right]$$

$_1Q_2 = 2892$

$H_p' - H_p = 59,929 - 2892 = 57,037$

$H_p' = 370,440 \times 1.8 \times 0.99842 = 665,730$

$H_p = 665,730 - 57,037 = 608,693$

Results for the lower heating value of ethane (C_2H_6) at constant pressure and 62 degrees F

Thomsen	608,693
Berthelot	613,993

Weighing Thomsen's value 2, and Berthelot's 1, we get for the average lower heating value

$H_p = 610,460$ B.T.U. per molat 62 degrees F. and const.press.

VII. Benzene vapor: (C_6H_6)

For the heat of combustion of benzene vapor the experimental value of Stohman, Rodatz and Herzberger which is 10,096 cal. per gram at 17 degrees C. is chosen as the best available. It is the average of 12 experiments. The method used was to pass a current of air over a wad of cotten saturated with benzene liquid and burning the resulting mixture of vapor and air in a constant pressure calorimeter. The products of combustion were led through a long spiral tube and then thru absorbers to remove the moisture in the usual way.

Calculation of the lower heating value: We shall assume that the oxygen and benzene in the benzene-air mixture are present in the theoretical proportions for combustion. The reaction equation is $C_6H_6 + 7.5O_2 + 28.5N_2 \rightarrow 6CO_2 + 3H_2O + 28.5N_2$ The partial pressure of the benzene vapor in the original mixture is $1/37 \times 14.7 = 0.40$ lb. per sq. in. According to Young* the saturation pressure of benzene vapor at 17 degrees C. is 65 mm. Hg, or 1.25 lb. per sq. in. Since the assumed partial pressure of the benzene vapor in the initial mixture is only about one third of the saturation pressure of benzene, at 17 degrees C., the assumed partial pressure can be easily attained and is reasonable.

The partial pressure of the water vapor in the products of combustion considered non-condensed is

$= 3/37.5 \times 14.7 = 1.176$ lb. per sq. in.

*Young. Scientific Proceedings Royal Dublin Society. Series 2. v.12. p.422. (1910)

Saturation temperature at this pressure is 107 degrees F.

$i_1'' = 1107.7$ $\quad i_1' = 30.1$ (at 17 degrees C. = 62 degrees F.)

$Q_2' = 54(1107.7 - 30.1) = 58190$ B.T.U. per mol benzene.

$Q_2 = 1,050$

$H_p' - H_p = 58,190 - 1050 = 57140$

$H_p = 78.05 \times 10,096 \times 1.8 \times 0.99842 = 1,416,460$

$H_p = 1,416,460 - 57,140 = 1,359,320$ B.T.U.per mol at 62° F.

VIII. Amorphous Carbon

We have the following experimental data available for the heating value of amorphous carbon:

Date	Investigator.	Value, cal. per gram.
1848	Andrews	7,678
1852	Favre and Silbermann	8,080
1883	Gottlieb	8,033
1889	Berthelot	8,137

Andrews states in his discussion of the value given above, which is the average of eight determinations with highly pureified wood charcoal in the bomb calorimeter, that in spite of the presence of excess oxygen, carbon monoxide was found in the products of combustion. This fact, of course, renders his value too low.

Favre and Silbermann also found carbon monoxide in the products of combustion from their experiments. After determining the amount of carbon monoxide present in any one case they added to the observed result the heat of combustion of this given amount of carbon monoxide so that their final results give the heat of combustion of carbon to carbon dioxide. This

correction in their case amounts to only about three percent, so that errors introduced by using an incorrect value for the heat of combustion of carbon monoxide are insignificant. Eighteen experiments in three series were run using highly purified wood charcoal. The values of the first series consisting of five experiments showed a maximum variation of 89 calories in the values given for the heat of combustion per gram. The average value from the first series is 8,086 calories per gram. The next seven experiments constituting the second series showed a maximum variation of 31 calories. The average of the second series is 8,081 calories per gram. In the last six experiments wood charcoal purified in different ways was used in different determinations to note if the method of purification had any effect on the results. In this last series the maximum variation between any two results was 19 calories and the average of these six was 8,080 calories per gram. This is the result quoted above.

Gottlieb used a calorimeter very similar to the one used by Favre and Silbermann. The carbon used by Gottlieb was prepared by heating a five-gram ball of cotton in a loosely covered dish slowly at first and then more intensely after all the combustible gases had been driven off. Later the cotton charcoal was transferred to a tightly covered platinum dish and heated to about 950 degrees C. for some hours and then cooled in a dessicator. This carbon absorbed moisture freely. Upon analysis the sample showed 1.5% moisture. It is safe to assume that only a portion of this moisture was absorbed by the time the sample for combustion was weighed and the rest was absorbed during the

time the calorimeter was being prepared for operation. With a slight amount of moisture present in the sample as weighed, of course, the final result calculated on the basis of this weight will be slightly low. Therefore, Gottlieb's result which is the average of six experiments which have a maximum variation of 7 calories per gram points to the accuracy of the Favre and Silbermann value.

Berthelot's value was obtained by burning wood charcoal, very carefully purified and dried. Oxygen under 25 atmospheres pressure was used in the bomb calorimeter to insure complete combustion. The value given above is the average of six experiments which show a maximum variation of 10 calories per gram.

Of the above values quoted we shall choose the Favre and Silbermann value which is substantiated by a total of 24 experiments in preference to that of Berthelot which is the result of only six experiments. Also, it is very possible that Berthelot's method of purification was at fault.

Reducing the Favre and Silbermann value, which is in terms of the 20 degree calorie, to mean B.T.U. per mol, we have for the heating value of amorphous carbon at 62 degrees F:

H = 174,250 B.T. U. per mol at 62 degrees Fahrenheit.

Table of Heats of Combustion

No.	Reaction	Lower heat of combustion at constant pressure and 62 degrees F. in mean B.T.U.		
		per mol.	per lb.	per cu.ft.
1.	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	103,450	51,725	271.8
2.	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	122,130	4,361.8	320.9
3.	$H_2 + CO_2 \rightarrow H_2O + CO$	-18,680	------	----
4.	C(amorp)$+ CO_2 \rightarrow 2CO$	-70,010	------	----
5.	C " $+ O_2 \rightarrow CO_2$	174,250	14,521	----
6.	C " $+ 2H_2 \rightarrow CH_4$	35,380	------	----
7.	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	345,770	21,568	908.5
8.	$C_2H_2 + 2\frac{1}{2}O_2 \rightarrow 2CO_2 + H_2O$	542,110	20,838	1,424.4
9.	$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$	575,210	20,520	1,511.4
10.	$C_2H_6 + 3\frac{1}{2}O_2 \rightarrow 2CO_2 + 3H_2O$	610,460	20,316	1,604.0
11.	C_6H_6(vapor)$+ 7\frac{1}{2}O_2 \rightarrow 6CO_2 + 3H_2O$	1,359,320	17,415	3,571.5

Table of Heats of Combustion - continued.

No.*	Lower heat of combustion at constant volume and 62 degrees F. in mean B.T.U.			Heat of combustion at absolute zero in mean B.T.U. per mol.
	Per mol	Per lb.	Per cu.ft.	
1.	102,930	51,564	270.4	102,100
2.	121,610	4,343.2	319.5	121,250
3.	-18,680	------	-----	-19,150
4.	-68,970	------	-----	-68,430
5.	174,250	14,521	-----	174,060
6.	34,340	------	------	31,250
7.	345,770	21,568	908.5	347,020
8,	541,590	20,838	1,423.0	541,600
9.	575,210	20,520	1,511.4	576,730
10.	610,980	20,333	1,605.3	613,520
11.	1,359,840	17,423	3,572.9	1,364,370

* For reactions corresponding to these numbers see table on p.119.

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APPENDIX C

CHEMICAL EQUILIBRIUM.

Appendix C

Chemical Equilibrium

A brief outline of the methods used in determining the equilibrium composition resulting from gaseous reactions at high temperature is given in the following. The experimental data used in determining the thermodynamically indeterminate constant of integration in the equilibrium equation is given for each of the reactions studied. For detailed descriptions and discussions of the experimental methods see Haber's "Thermodynamics of Technical Gas Reactions" and Nernst's "Theoretical Chemistry".

I. Streaming Method. The gases involved in the reaction are passed through a tube a section of which is heated to the desired temperature and the following section kept at a low temperature. The gases are assumed to attain equilibrium in the hot portion of the tube and to be cooled so rapidly in the cold portion of the tube that the reaction immediately stops. The equilibrium composition of the gases at the high temperature thus exists in the cooled gases which can then be easily analyzed.

II. Semipermeable Membrane Method. A vessel which is permeable to one constituent only of the reaction is evacuated and the reacting mixture of gases at the desired temperature caused to circulate around the outside of the vessel. The partial pressure of the one constituent to which the vessel is permeable will soon exist inside the vessel and can be measured with a manometer. This method is applicable only to a study of

the dissociation of H_2O since semipermeable substances are known for hydrogen only and are palladium, platinum, and iridium.

III. Maximum Explosion Pressure Method. The original mixture of gases is exploded in a closed vessel and the maximum pressure of explosion measured. Since the maximum pressure is dependant on the heat of reaction and the heat of reaction on the equilibrium composition the equilibrium composition lends itself to calculation from the maximum pressure. Also in those reactions which incur a change in the number of mols the maximum pressure is directly influenced by the equilibrium composition.

IV. Method of the Heated Catalyst. (a) If a catalyst such as a platinum wire is heated electrically in an atmosphere of gas the equilibrium composition of the gas, at the temperature of the wire, will exist in the gas immediately surrounding the wire. Due to the circulation of the gas set up by the heated wire the gas in contact with the wire will be swept into the cooler regions and the reaction thereby "frozen". This process is allowed to continue until the composition of the whole gas volume becomes constant. This condition is determined by analyzing samples of gas from time to time. Temperatures are determined by the change in the electrical resistance of the wire.

(b) A variation of this method is to heat a vessel containing the catalyst to the desired temperature and then to lead the gases through the vessel or enclose them in the vessel until equilibrium is established. Samples are drawn out from time to time and analyzed.

V. Iridium Dust Method. Iridium dust is produced by heating strips of iridium electrically in various gases. The

quantity of dust produced is dependant on the nature of the gas and the temperature to which the iridium is heated. This method is especially applicable to the measurement of the dissociation of carbon dioxide. Nitrogen and pure carbon monoxide produce no appreciable amount of dust while oxygen produces large quantities of dust. The amount of dust produced by carbon dioxide at a given temperature of the iridium and at atmospheric pressure is assumed to be due to the oxygen liberated by the dissociation of the carbon dioxide. A mixture of nitrogen and oxygen is found which will produce the same amount of dust as the carbon dioxide under the same conditions. Assuming that the oxygen content of the two gases is the same the equilibrium composition of the carbon dioxide reaction is then known.

VI. Measurement of Equilibrium in the Bunsen Flame. The inner and outer cones of the Bunsen flame are separated by fitting a glass tube as an extension on the end of the burner, the glass tube being of some what larger diameter than that of the burner. A stopper is made to fit tightly in the annular space between the burner and the glass tube. The inner cone then burns on the end of the regular Bunsen burner tube which is now inside the glass tube while the outer cone burns on the end of the glass tube. Samples of gas are withdrawn from the space between the two cones and are assumed to be in equilibrium. Temperatures are measured with thermo-couples.

VII. Direct Determination of Equilibrium. (a) When one of the constituents in the reaction is a solid such as carbon this can be placed in a porcelain tube and the whole heated in an

electric furnace. The gas constituents are then passed thru the porcelain tube at a rate sufficiently slow to give time for equilibrium to be established. The products are then analyzed.

(b) Carbon in the form of rods is heated by an electric current in an atmosphere of the gas. Reaction occurs at the surface of the rod and is "frozen" when the reacting gases diffuse into the colder regions.

In either method VII (a) or (b) a catalytic agent such as platinum, nickle or cobalt may or may not be used.

(c) A study of the water gas equilibrium is made by passing water vapor over glowing coals and analyzing the resulting gases.

VIII. Equilibrium from Density Measurement. The dissociation of carbon dioxide can be measured by electrically heating a platinum bulb filled with carbon dioxide to a desired temperature and then dropping into the bulb a small piece of aluminum. Changes of volume are measured by the movement of a short thread of mercury in a horizontal capillary outlet tube fitted to the platinum bulb. The following reaction occurs:

$$2Al + 3CO_2 = Al_2O_3 + 3CO$$

According to this reaction no change in volume will occur if the carbon dioxide is undissociated and if the assumption is made that equal weights of carbon monoxide and carbon dioxide have the same volumes under similar conditions of pressure and temperature. If the carbon dioxide is dissociated, a change in the number of mols will occur with the above reaction which is proportional to the amount of dissociation and which can be measured by the change of volume.

The general expression representing the equilibrium state in any reaction is as follows:

$$4.571 \log_{10} Kp = \frac{Ho}{T} - 2.3026 \sigma' \log_{10} T - \tfrac{1}{2}\sigma'' T - 1/6 \sigma''' T^2 + C$$

Where σ' is equal to the sum of the constant terms in the instantaneous specific heat equations for constant pressure of the constituents of the original mixture minus the sum of the constant terms of the instantaneous specific heat equations for constant pressure of the constituents of the products of the reaction. Likewise σ'' is the summation of the coefficients of T in the instantaneous specific heat equations while σ''' is the summation of the coefficients of T^2 in the instantaneous specific heat equations.

The general expression for the heat of reaction at absolute zero is

$$H_o = H_p - T\left[\sigma' + \tfrac{1}{2}\sigma'' T + \tfrac{1}{3}\sigma''' T^2\right]$$

Where T is the absolute temperature at which H_p is determined.

Reaction

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$

Inserting the proper constants in the above general equilibrium equation we have

$$4.571 \log_{10} K_P = \frac{121250}{T} - 5.3881 \log_{10} T + 0.001335T - 0.08 \cdot 10^{-6} T^2 + C$$

$$K_P = \frac{P_{CO_2}}{P_{CO} \cdot P_{O_2}^{\frac{1}{2}}} = \frac{(x)\ (3-x)^{\frac{1}{2}}}{(1-x)^{\frac{3}{2}}} \cdot \left(\frac{1}{P}\right)^{\frac{1}{2}}$$

100 (1-x) = percent dissociation of CO_2

P = pressure in lbs. per sq. ft. abs.

T = temperature Fahr deg. abs.

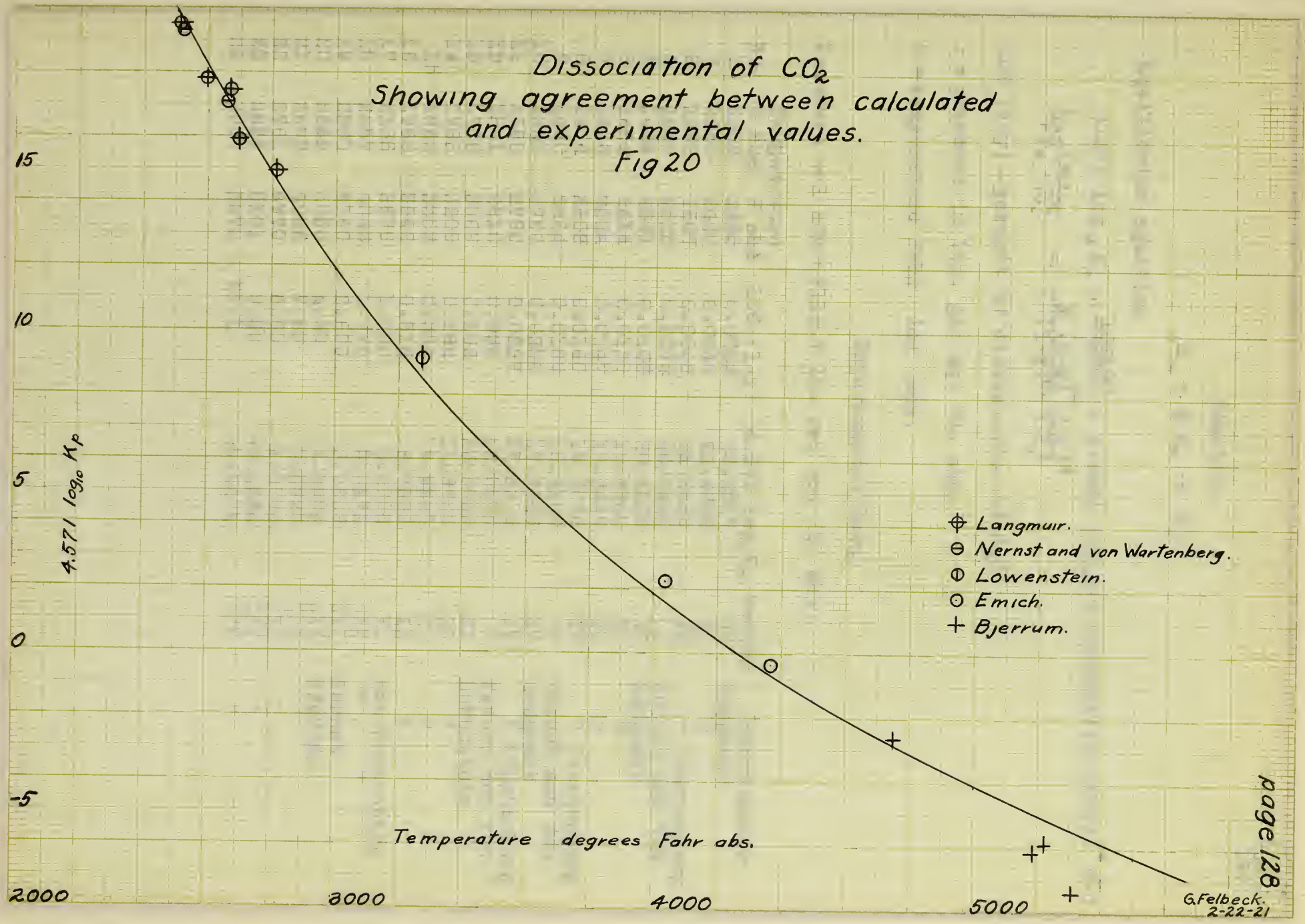
Experimental Data

Pressure = 1 atmosphere = 2116.7 lb. per sq. ft.

No.	Temperature C abs	F abs	100 (1-x)	4.571 $\log_{10} K_p$	Method	Investigator
1	1300	2340	0.00414	23.1374	I	Nernst and von Wartenberg
2	1395	2511	0.0142	19.4673	IV	Langmuir
3	1400	2520	0.01-0.02	19.3040	I	Nernst and von Wartenberg
4	1443	2597	0.025	17.7830	IV	Langmuir
5	1478	2660	0.029-0.035	17.0478	I	Nernst and von Wartenberg
6	1481	2666	0.0281	17.4361	IV	Langmuir
7	1498	2696	0.0471	15.9030	IV	Langmuir
8	1565	2817	0.064	14.9835	IV	Langmuir
9	1818	3272	0.45	9.1254	VIII	Lowenstein
10	2243	4037	4.50	2.2520	V	Emich
11	2423	4361	10.50	-0.3710	V	Emich
12	2640	4752	21.00	-2.6343	III	Bjerrum
13	2879	5182	51.70	6.1644	III	Bjerrum
14	2900	5220	49.20	-5.9265	III	Bjerrum
15	2945	5301	64.70	-7.4047	III	Bjerrum
16	3116	5609	76.10	-8.6202	III	Bjerrum

Taking C = -13.1 in the above equation for equilibrium we have the following calculated values. The agreement between calculated and experimental results can be seen from fig. (20) page 128.

Temp Fahr abs	4.571 $\log_{10} K_p$	Temp Fahr abs	4.571 $\log_{10} K_p$
2300	24.146	4000	1.855
2500	19.925	4500	-1.462
3000	11.861	5000	-4.116
3500	6.134	5500	-6.297


Dissociation of CO_2
Showing agreement between calculated and experimental values.
Fig 20
15
10
5
0
-5
4.571 log10 Kp
Langmuir.
Nernst and von Wartenberg.
Lowenstein.
Emich.
Bjerrum.
Temperature degrees Fahr abs.
2000
3000
4000
5000
G.Felbeck.
2-22-21

Dissociation of CO_2

Showing calculated pressure from experimental values

Fig 50

Reaction

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O$$

Equilibrium equation

$$4.571 \log_{10} K_p = \frac{102100}{T} - 6.2631 \log_{10} T + 0.0002361T + 0.0333 \cdot 10^{-6} T^2 + C$$

$$K_p = \frac{P_{H_2O}}{P_{H_2} \cdot P_{O_2}^{1/2}} = \frac{y\,(3-y)^{\frac{1}{2}}}{(1-y)^{3/2}} \cdot \left(\frac{1}{P}\right)^{\frac{1}{2}}$$

100 (1-y) = percent of dissociation of H_2O

P = pressure in lbs. per sq. ft. abs.

T = temperature Fahr. deg. abs.

Experimental Data

Pressure = 1 atm = 2116.7 lb. per sq. ft. abs.

No.	Temperature C abs	Temperature F abs	100 (1-y)	$4.571 \log_{10} K_p$	Method	Investigator
1	1325	2385	0.0033	23.2917	IV	Langmuir
2	1355	2439	0.0049	22.6355	IV	"
3	1393	2507	0.0068	21.6458	IV	" (Wartenberg
4	1397	2515	0.0078	20.8400	I	Nernst and voh
5	1434	2581	0.0103	20.4235	IV	Langmuir
6	1452	2614	0.0137	19.5740	IV	"
7	1458	2624	0.0147	19.3647	IV	"
8	1474	2653	0.0140	19.5096	IV	" (Wartenberg
9	1480	2664	0.0189	18.6160	I	Nernst and von
10	1531	2756	0.0255	17.7240	IV	Langmuir
11	1550	2790	0.0287	17.3276	IV	" (Wartenberg
12	1561	2810	0.034	16.8670	I	Nernst and von
13	1705	3069	0.102	13.5950	II	Lowenstein
14	1783	3209	0.182	11.8700	II	"
15	1863	3353	0.354	9.9320	II	"
16	1968	3542	0.518	8.7505	II	"
17	2155	3879	1.180	6.2900	II	von Wartenberg
18	2257	4063	1.770	5.0271	II	" "
19	2300	4140	2.600	3.9608	III	Nernst
20	2642	4756	4.30	2.3904	III	Bjerrum
21	2698	4856	7.50	0.6820	III	"
22	2761	4970	6.60	1.0776	III	"
23	2834	5101	9.80	-0.1534	III	"
24	2929	5272	11.1	-0.5471	III	"

Taking C = 1.1 in the equilibrium equation we have the following calculated values. The agreement between calculated and experimental results is seen from Fig (21) page 131.

Temp Fahr abs.	$4.571 \log_{10} K_p$
2500	21.457
3000	14.365
3500	9.309
4000	5.542
4500	2.646
5000	0.366
5500	-1.455

Reaction

$$H_2 + CO_2 \rightleftarrows H_2O + C\ O$$

By subtracting the equilibrium equation for the reaction $CO + \frac{1}{2} O_2 \rightarrow CO_2$ from the equilibrium equation for the reaction $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ we get the equilibrium equation for the above reaction which is

$$4.571 \log_{10} K_p = \frac{-19150}{T} - 0.8750 \log_{10} T - 1.0970 \cdot 10^{-3} T + 0.1133\, 10^{-6} T^2 + 14.2$$

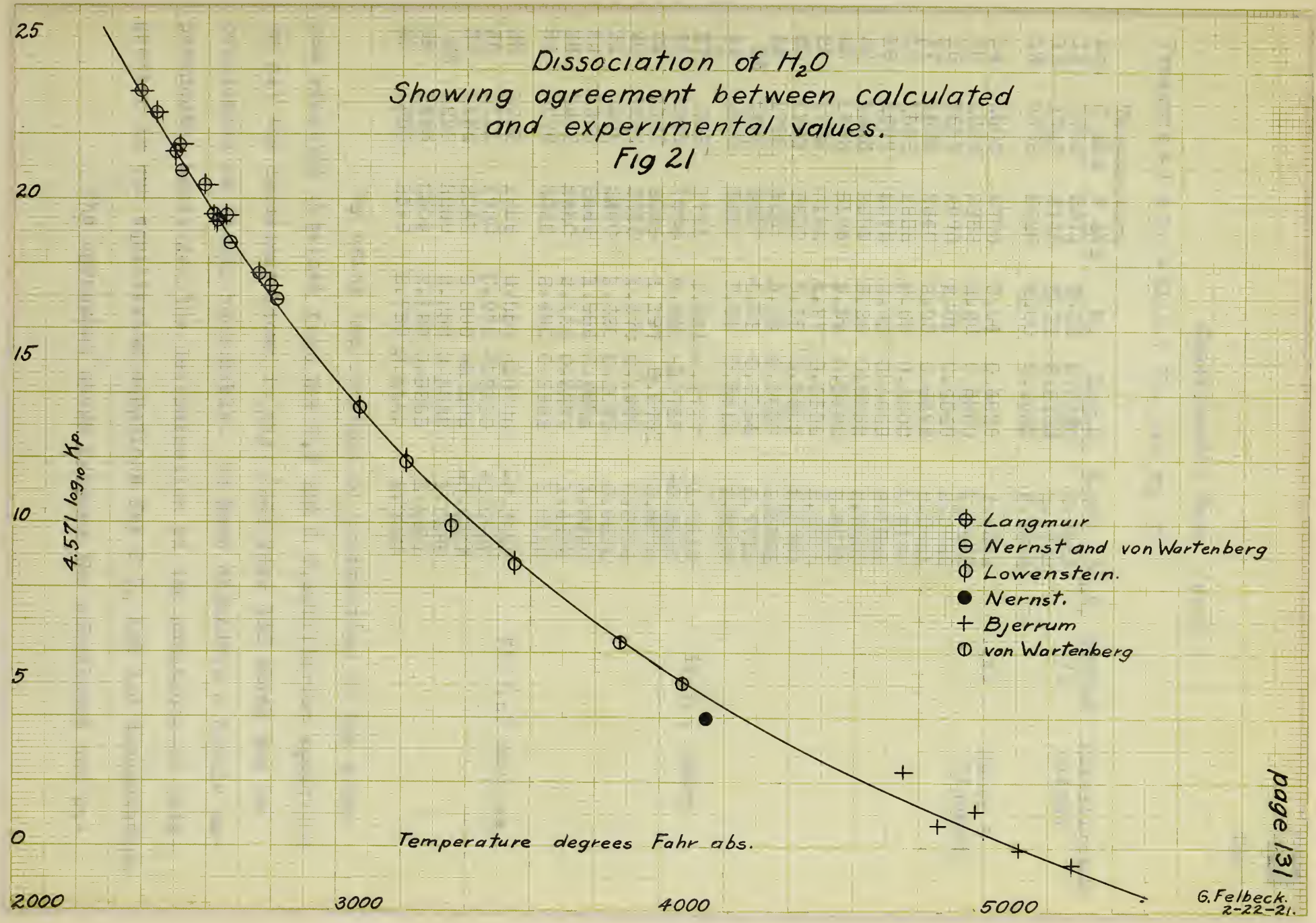
$$K_p = \frac{P_{H_2O} \cdot P_{CO}}{P_{H_2} \cdot P_{CO_2}} = \frac{y\,(1-x)}{x\,(1-y)}$$

Experimental Data

Pressure = 1 atm = 2116.7 lb. per sq. ft.

No.	Temperature C abs	Temperature F abs	K_p	$\text{Log}_{10} K_p$	$4.571 \log_{10} K_p$	Method	Investigator
1	1453	2617	2.39	0.3784	1.7276	VI	Allner
2	1507	2715	2.46	0.3909	1.7868		
3	1519	2735	2.62	0.4183	1.9121		
4	1547	2787	2.31	0.3636	1.6620		
5	1553	2795	2.25	0.3522	1.6099		
6	1579	2842	2.69	0.4299	1.9651		
7	1619	2915	3.31	0.5198	2.3760		
8	1635	2944	3.10	0.4914	2.2462		
9	1659	2987	3.59	0.5551	2.5374		
10	1703	3065	3.13	0.4955	2.2649		

Dissociation of H_2O
Showing agreement between calculated and experimental values.
Fig 21



page 131

G. Felbeck.
2-22-21.

Fig 51

Chromic oxide adsorption isotherm, Adams' gel

Chromic oxide adsorbed, millimoles per gram

pH to neutralize adsorbed chromic oxide

Experimental Data (cont.)

Pressure = 1 atm = 2116.7 lb. per sq. ft.

No.	Temperature C abs	Temperature F abs	K_p	$\log_{10} K_p$	4.571 $\log_{10} K_p$	Method	Investigator
11	1706	3071	3.26	0.5132	2.3458	VI	Allner
12	1747	3145	3.31	0.5198	2.3760		
13	1798	3238	4.00	0.6021	2.7522		
14	1503	2705	3.04	0.4829	2.2073	VI	Haber & Richardt
15	1528	2752	2.66	0.4250	1.9422		
16	1538	2770	2.85	0.4548	2.0789		
17	1578	2840	2.80	0.4472	2.0441		
18	1586	2856	2.63	0.4200	1.9198		
19	1597	2875	2.93	0.4669	2.1342		
20	1643	2959	3.26	0.5132	2.3458		
21	1763	3174	3.39	0.5302	2.4235		
22	1773	3192	4.27	0.6304	2.8816		
23	1783	3210	3.65	0.5629	2.5730		
24	1795	3231	3.68	0.5658	2.5862		
25	1798	3237	4.04	0.6064	2.7718		
26	1824	3282	3.64	0.5515	2.5209		
27	959	1726	0.534	-0.2727	-1.2465	IV ($_b$)	Hahn
28	1059	1906	0.840	-0.0757	-0.3460		
29	1159	2086	1.197	0.0781	0.3570		
30	1259	2266	1.570	0.1959	0.8954		
31	1278	2300	1.620	0.2095	0.9576		
32	1359	2446	1.956	0.2914	1.3320		
33	1478	2660	2.126	0.3276	1.4974		
34	1678	3020	2.490	0.3962	1.8110		
35	1031	1856	0.850	-0.0706	-0.3227	VII (c)	Harries
36	1111	1920	0.975	-0.0110	-0.0503		
37	1134	2041	0.890	-0.0506	-0.2313		
38	1227	2209	2.250	0.3522	1.6100		
39	1283	2309	2.120	0.3263	1.4915		
40	1333	2399	2.780	0.4440	2.0295		

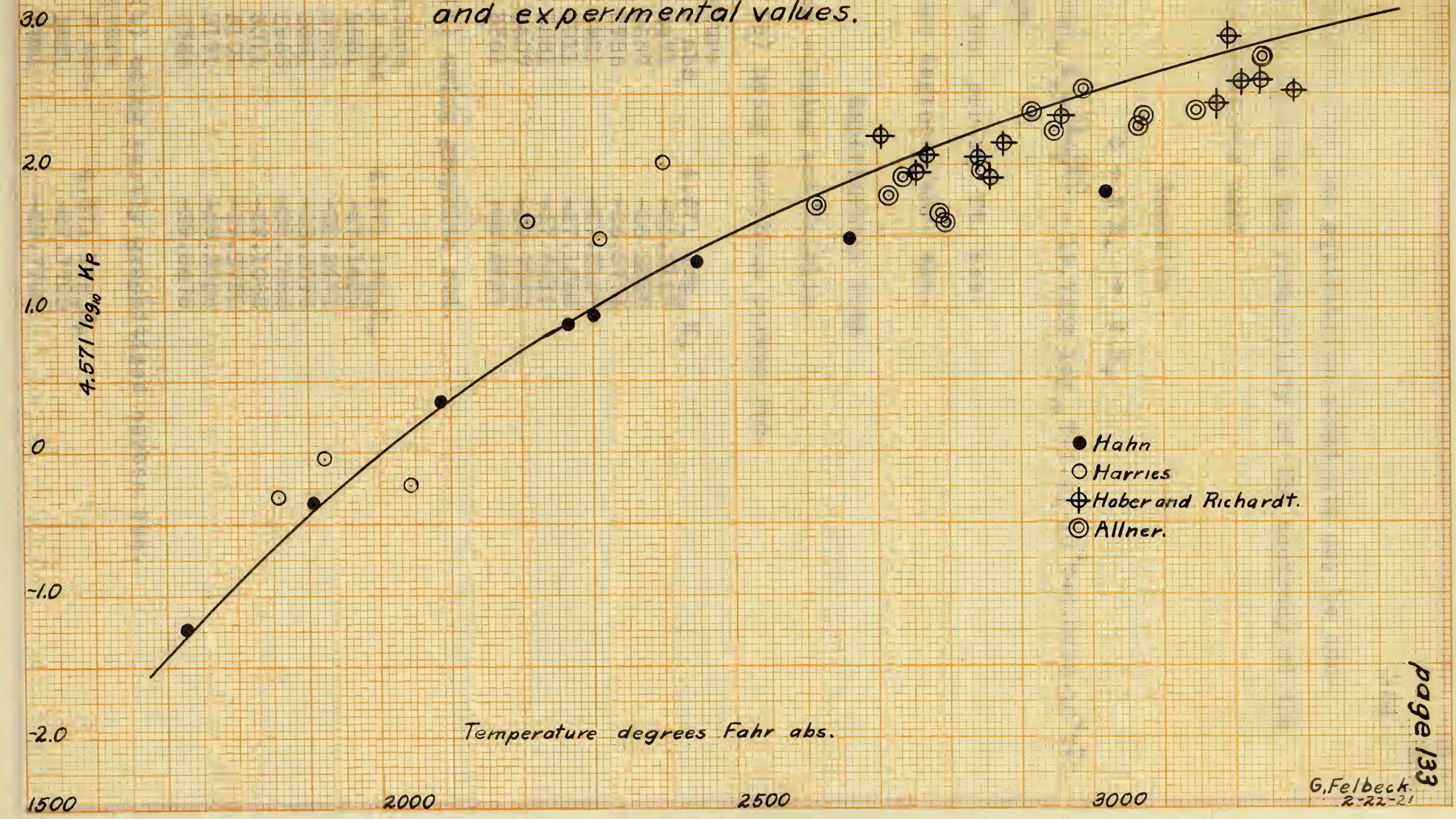
By using the constant of integration in the water gas reaction obtained from the H_2O and C O_2 equilibrium equations we get the agreement shown in fig. (22) page 133 which can be considered as fairly reasonable. We have therefore a double experimental basis for the determination of the constants of integration in our equilibrium equations for C O_2 and H_2O dissociation.

The agreement shown between the calculated and ex-

Fig 22

Equilibrium of the Reaction $H_2 + CO_2 \rightleftarrows H_2O + CO$

Showing agreement between calculated and experimental values.



G. Felbeck.
2-22-21

Fig 55
CO + OH ⇌ CO2 + H activation energy 4.5 kcal
Extrapolation assumed due to curvature
Solid line by Wolfram & Dodd
Temperature degrees Kelvin
Allen
Hansen
Thompson & Hinshelwood
Smith

perimental results for the equilibrium constants may be considered also to increase the probability of the accuracy of the specific heat equations used.

Reaction

$$C + 2H_2 \rightarrow CH_4$$

$$4.571 \log_{10} K_p = \frac{31,250}{T} - 19.7333 \log_{10} T + 1.21 \cdot 10^{-3} T + 0.0293 \cdot 10^{-6} T^2 + C$$

$$K_p = \frac{P_{CH_4}}{P^2_{H_2}}$$

P = pressure lbs. per sq. ft. abs.

T = temperature degrees Fahr. abs.

Experimental Data

Investigators - Pring and Fairlie.

Method VII (b) using amorphous carbon rod.

No.	Temperature C abs.	F abs	$4.571 \log_{10} K_p$
1	1373	2471	-26.2129
2	1493	2687	-26.2855
3	1548	2786	-26.3774
4	1623	2921	-27.3137
5	1673	3011	-27.1358
6	1823	3281	-27.6615
7	1893	3407	-29.9960
8	1973	3551	-28.5527

Method VII (b) using graphite rod.

No.	Temperature C abs.	F abs	$4.571 \log_{10} K_p$
9	1473	2651	-27.1439
10	1548	2786	-28.2491
11	1573	2831	-28.3096
12	1648	2966	-28.7588
13	1673	3011	-29.1065
14	1723	3101	-29.3750
15	1773	3191	-29.3956
16	1848	3326	-29.8478

Method VII (b) using partly graphitized carbon rod.

No.	Temperature C abs.	F abs.	$4.571 \log_{10} K_p$
17	1573	2831	-27.7700
18	1623	2921	-27.7700

Method VII (b) using partly graphitized carbon rod. (cont.)

No.	Temperature C abs	Temperature F abs	$4.571 \log_{10} K_p$
19	1723	3101	-27.6827
20	1748	3146	-28.9150
21	1813	3263	-29.2140

Investigators - Mayer and Altmayer.

Method VII (a) Passing hydrogen over sugar carbon deposited on nickle or cobalt as catalyser.

No.	Temperature C abs	Temperature F abs	$4.571 \log_{10} K_p$
1	748	1346	-11.9020
2	780	1404	-13.5529
3	809	1456	-13.8736
4	840	1512	-14.3885
5	850	1530	-15.7218
6	880	1584	-16.3191
7	898	1616	-17.3384

Investigators - Clement and Adams.

Method VII (a) Passing superheated steam over coke.

No.	Temperature C abs	Temperature F abs	$4.571 \log_{10} K_p$
1	1173	2110	-26.4310
2	1273	2290	-26.5390
3	1373	2470	-29.5910
4	1473	2650	-29.9150
5	1573	2830	-29.0260

Note: In cases where several values for the equilibrium constant were given by the investigator for any one temperature the average has been taken and is quoted here.

Putting C = 24.8 in the equilibrium equation we get the following calculated values:

Temperature Fahr abs	$4.571 \log_{10} K_p$
1300	-10.9843
1500	-15.1595
1750	-19.1267
2000	-22.1793
2250	-24.5915
2500	-26.5471
2750	-28.1577
3000	-29.5068
3250	-30.6473

The constant 24.8 places the calculated curve through the Mayer and Altmayer points and between the Clement and Adams and Pring and Fairlie points as shown in fig. (23) page 137. Considering the fact that the specific heat equation used for methane is based on low temperature measurements only the agreement obtained with the equilibrium curve is very good.

Reaction $C + CO_2 \rightarrow 2CO$

Equilibrium equation is

$$4.571 \log_{10} K_p = \frac{-68,430}{T} + 9.1874 \log T - 1.9844 \cdot 10^{-3} T + 0.109 \cdot 10^{-6} T^2 + C$$

$$K_p = \frac{P_{CO}}{P_{CO_2}}$$

P = pressure lb. per sq. ft. abs. 1 atmosphere = 2116.7# per sq (ft

T = temperature degrees Fahr abs.

Experimental Data

No.	Temperature C abs	Temperature F abs	$4.571 \log_{10} K_p$	Method	Investigator
1	796	1433	4.0615	VII (a)	Mayer and Jacoby
2	1861	1550	8.5347	using	
3	896	1613	9.8218	sugar	
4	940	1692	11.9337	carbon.	
5	1043	1877	17.7770		
6	1091	1964	19.3503		
7	1073	1931	14.1329	VII (a)	Clement and Adams
8	1123	2021	16.6544	using	
9	1173	2111	18.7188	charcoal	
10	1198	2156	19.6607		
11	1273	2291	20.5041		
12	1373	2471	22.1132		
13	1173	2111	18.7995	VII (a)	Clement and Adams
14	1273	2291	19.0320	using	
15	1373	2471	21.9055	coke	
16	1473	2651	23.7709		
17	1573	2831	26.1465		
18	923	1661	12.4445	VII (a)	Boudouard
19	1073	1931	20.1926		
20	1198	2156	21.4296		
21	1073	1931	18.5127	VII (a)	Rhead and Wheeler
22	1123	2021	20.4567		
23	1173	2111	22.2460		
24	1223	2201	23.4972		
25	1273	2291	24.9294		

Fig 23

Equilibrium of the Reaction $C+2H_2 \rightleftharpoons CH_4$
Showing agreement between calculated and experimental values.

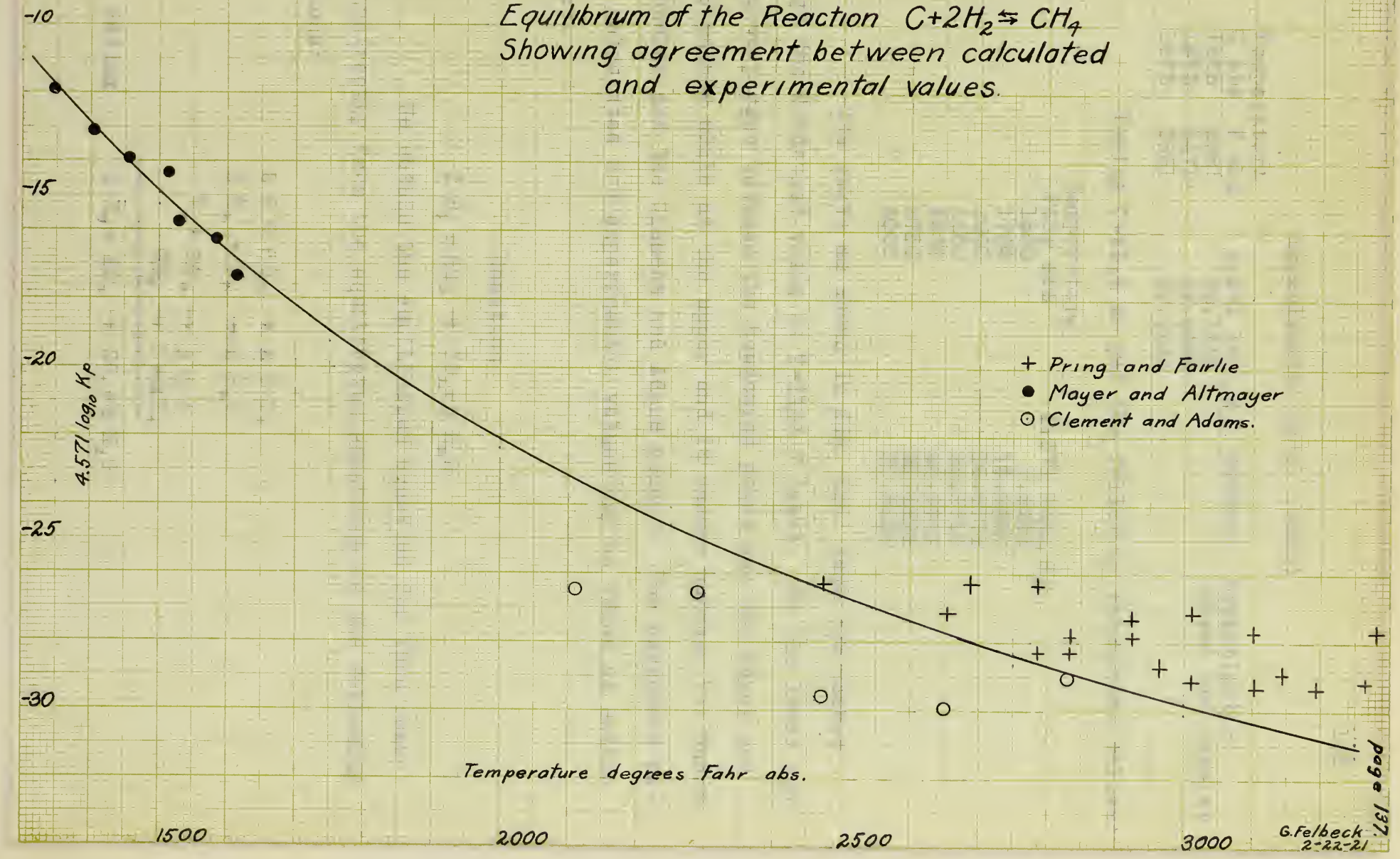


Fig 23

Estimation of the heat of reaction $C_4H_8 \rightleftharpoons CH_4 + C_3H_4$ by the method of Temkin and Pyzhev

Equilibrium constant K_p plotted against reciprocal of absolute temperature

Open circles: data of Kassel

Crosses: data of Hurd and Spence

Filled circles: data of Hurd and Blunck

Experimental Data (cont)

No.	Temperature C abs	F abs	$4.571 \log_{10} K_p$	Method	Investigator
26	1323	2381	26.1162		Rhead and Wheeler
27	1373	2471	27.5758		
28	1473	2651	29.9264		

Taking C=26.4 we get the following calculated values:

Temperature Fahr abs	$4.571 \log_{10} K_p$
1500	7.2275
1750	13.9589
2000	18.9799
2250	22.8715
2500	25.9767
2750	28.4822
3000	30.5638

The curve as shown in fig. (24) page 139 passes through the Bondourad value at T=2156 F (abs). At the lower end the curve passes between the Boudourad point and the Mayer and Jacoby points while at the upper end it passes between the Rhead and Wheeler and the Clement and Adams points. The agreement between calculated and experimental values may be taken as satisfactory.

Reaction

$$C H_4 + 2O_2 \rightarrow CO_2 + 2 H_2O$$

We obtain the equilibrium equation for this reaction indirectly from the equilibrium equations of the following reactions:

$$2 C O + O_2 \rightarrow 2 C O_2$$
$$2 H_2 + O_2 \rightarrow 2 H_2O$$
$$C + CO_2 \rightarrow 2 C O$$
$$CH_4 \rightarrow C + 2H_2$$

Adding $$C H_4 + 2O_2 \rightarrow CO_2 + 2 H_2O$$

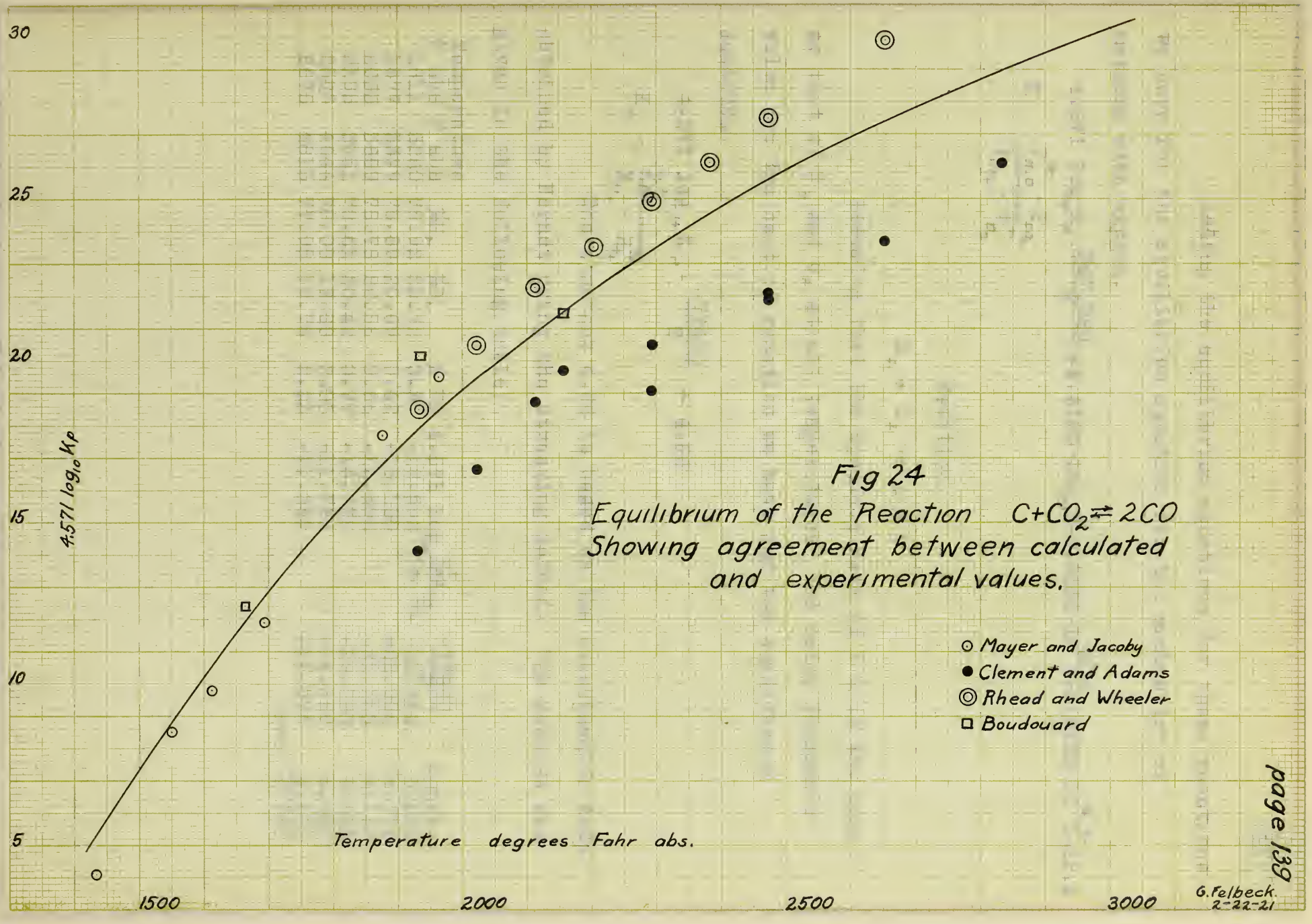


Fig 24

Equilibrium of the Reaction $C+CO_2 \rightleftharpoons 2CO$
Showing agreement between calculated and experimental values.

G. Felbeck.
2-22-21

Fig 2.4

Equilibrium relationship between $CaCO_3$ precipitation reaction and pH value

Curves obtained from experimental data

Adding the equilibrium equations for these reactions we have for the equilibrium equation for the combustion of methane with oxygen.

$$4.571 \log_{10} K_p = \frac{347,020}{T} + 5.6183 \cdot \log_{10} T - 0.0552 \cdot 10^{-3} T - 0.0133 \cdot 10^{-6} T^2 - 22.4$$

$$K \quad \frac{P^2_{H_2O} \cdot P_{CO_2}}{P_{CH_4} \cdot P^2_{O_2}}$$

Reaction

$$N_2 + O_2 \rightarrow 2\,N\,O$$

Assuming that the specific heat of N O is the same as that of N_2 and O_2 at all temperatures, and using Thomsen's value for the heat of reaction we have for the equilibrium equation:

$$4.571 \log_{10} K_p = \frac{-77400}{T} + 4.86$$

$$K_p = \frac{P^2_{NO}}{P_{N_2} \cdot P^{1/2}_{O_2}}$$

The constant 4.86 is based on the experimental data obtained by Nernst using the streaming method. The results are given in the following table:

Temperature C abs	Temperature F abs	$\%N_2$	$\%O_2$	% NO	$4.571 \log_{10} \frac{P^2_{NO}}{P_{N_2} P_{O_2}}$	$\frac{-77400}{T}$	Const.
1811	3260	78.92	20.72	0.37	-18.592	-23.742	5.150
1877	3379	78.89	20.69	0.42	-18.130	-22.906	4.776
2033	3659	78.78	20.58	0.64	-16.406	-21.153	4.747
2195	3951	78.61	20.42	0.97	-14.738	-19.590	4.852
2580	4644	78.08	19.88	2.05	-11.736	-16.667	4.931
2675	4815	77.98	19.78	2.23	-11.389	-16.074	4.685
						ave.	4.858

Equilibrium Equations

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O.$

$$4.571 \log_{10} K_p = \frac{102100}{T} - 6.2631 \log_{10} T + 0.2361 \cdot 10^{-3} T + 0.033 \cdot 10^{-6} T^2 + 1.1$$

$CO + \frac{1}{2}O_2 \rightarrow CO_2$

$$4.571 \log_{10} K_p = \frac{121250}{T} - 5.3881 \log_{10} T + 1.3335 \cdot 10^{-3} T - 0.08 \cdot 10^{-6} T^2 - 13.1$$

$H_2 + CO_2 \rightarrow H_2O + CO$

$$4.571 \log_{10} K_p = \frac{-19150}{T} - 0.8750 \log_{10} T - 1.0970 \cdot 10^{-3} T + 0.1133 \cdot 10^{-6} T^2 + 14.2$$

$C + 2\,H_2 \rightarrow CH_4$

$$4.571 \log_{10} K_p = \frac{31250}{T} - 19.7333 \log_{10} T + 1.21 \cdot 10^{-3} T + 0.029 \cdot 10^{-6} T^2 + 24.8$$

$C + CO_2 \rightarrow 2\,CO$

$$4.571 \log_{10} K_p = \frac{-68430}{T} + 9.1874 \log_{10} T - 1.9844\ 10^{-3} T + 0.109 \cdot 10^{-6} T^2 + 26.4$$

$C\,H_4 + 2O \rightarrow CO_2 + 2 \cdot H_2O$

$$4.571 \log_{10} K_p = \frac{347020}{T} + 5.6183 \log_{10} T - 0.0552 \cdot 10^{-3} T - 0.0133 \cdot 10^{-6} T^2 - 22.4$$

$N_2 + O_2 \rightarrow 2\,NO$

$$4.571 \log_{10} K_p = \frac{-77400}{T} + 4.86$$

References for Experimental Data on Reaction $CO + \frac{1}{2}O_2 \rightarrow CO_2$

1. Nernst and von Wartenberg — Zeit Phys Chem — 56-548 (1906)
2. Langmuir — Jour Am Chem Soc — 28-1357 (1906)
3. Lowenstein — Zeit Phys Chem — 54-707 (1906)
4. Emich — Monatshefte f Chem — 26-1011 (1905)
5. Bjerrum — Zeit Phys Chem — 79-357 (1906)

References for Experimental Data on equilibrium in Reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

1. Langmuir — Jour Am Chem Soc — 28-1357 (1906)
2. Lowenstein — Zeit Phys Chem — 54- 715 (1906)
3. von Wartenberg — Zeit Phys Chem — 56- 513 (1906)
4. Nernst — Zeit Anorg Chem — 45- 130 (1905)
5. Nernst and von Wartenberg — Zeit Phys Chem — 56- 534 (1906)
6. Bjerrum — Zeit Phys Chem — 79- 513 (1912)
7. Seigel — Zeit Phys Chem — 87- 641 (1914)

References for Experimental Data on equilibrium in Reaction $H_2 + CO_2 \rightarrow H_2O + CO$

1. Allner — Jour f Gasbel — 48 (1905) pp 1035, 1057, 1081, 1107.
2. Haber and Richardt — Zeit Anorg Chem — 38- 5 (1904)
3. Hahn — Zeit Phys Chem — 42- 705 (1902-3)
4. Harries — Jour f Gasbel — 37- 82 (1894)

References for Equilibrium Data on Reaction $C + 2H_2 \rightarrow CH_4$

1. Pring and Fairlie — Jour Chem Soc — 101- 91 (1912)
2. Mayer and Altmeyer — Berlin Ber — 40-2135 (1907)
3. Clement and Adams — U S Bureau of Mines — Bul # 7 p 41 (1911)

References for Reaction $C + CO_2 \rightarrow 2CO$

1. Mayer and Jacoby — Jour f Gasbel — 52 (1909) 282, 305
2. Clement and Adams — U.S. Bureau of Mines — Bul # 7 (1909)
3. Boudourad — Compt Rendus — 130-132 (1900)
4. Rhead and Wheeler — Jour Chem Soc — 97 (1910) 2178
   " " " — 89 (1911) 1140

References for Equilibrium Data for Reaction $N_2 + O_2 \rightarrow 2NO$

1. Nernst — Zeit f Anorg Chem — 49 213 (1906)

A P P E N D I X D

DETERMINATION OF THE MAXIMUM POSSIBLE PERCENTAGE OF N O PRESENT AT THE POINT OF MAXIMUM TEMPERATURE IN THE GAS ENGINE

Appendix D

To determine the maximum percent of N O present at the point of maximum temperature in the gas engine.

The equilibrium equation is

$$4.571 \log_{10} \frac{P^2_{NO}}{P_{N_2} \cdot P_{O_2}} = \frac{-77400}{T} + 4.86$$

$$P^2_{N_2} = P_{N_2} \cdot P_{O_2} \cdot K_p \qquad (A)$$

In order to make the partial pressure of the N O as large as possible the partial pressures of N_2 and O_2 must be as large as possible for a given value of K_p.

Assuming a gaseous mixture with 50% excess air and a dissociation of 10% at the point of maximum temperature the N_2 and O_2 will be present in the ratio of 9.5 volumes of N_2 to 1 vol. of O_2.

Let V = % of N_2 transformed to N O

Then at equilibrium point the mixture is

		mols
N O	= 2 x 9.5 V	= 19 V
N_2	= 9.5 (1-V)	= 9.5 - 9.5 V
O_2	= 1-9.5 V	= 1 - 9.5 V

M = Total number of mols present

$$P_{NO} = \frac{19\,V}{M} \cdot P \;,\quad P_{N_2} = \frac{9.5\,(1-V)}{M} \cdot P \;,\quad P_{O_2} = \frac{1-9.5\,V}{M} \cdot P$$

Substituting the expressions for partial pressure in equation (A) we have

$$(19\,V)^2 = 9.5\,(1-V) \cdot (1-9.5\,V) \cdot K_p$$

Solving for V

$$V = \frac{-10.5 \pm \sqrt{72.25 + \frac{15.2}{K_p}}}{\frac{76}{K} - 19}$$

Taking T = 5000 F (abs) a liberal maximum temperature K_p = 0.00477.

Solving equation (B)

$V = 0.0064$

That is 0.64% of the nitrogen present is transformed into N O under the most favorable conditions. Decreasing the maximum temperature and the amount of excess air will both decrease the value of V.

The accuracy of the physical and chemical constants used in this discussion does not warrant the consideration of a quantity which amounts to less than 0.64% of the total gas volume present. No appreciable error will be introduced into the calculations of the equilibrium conditions by neglecting the reaction

$$N_2 + O_2 \rightarrow 2\ N\ O.$$

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